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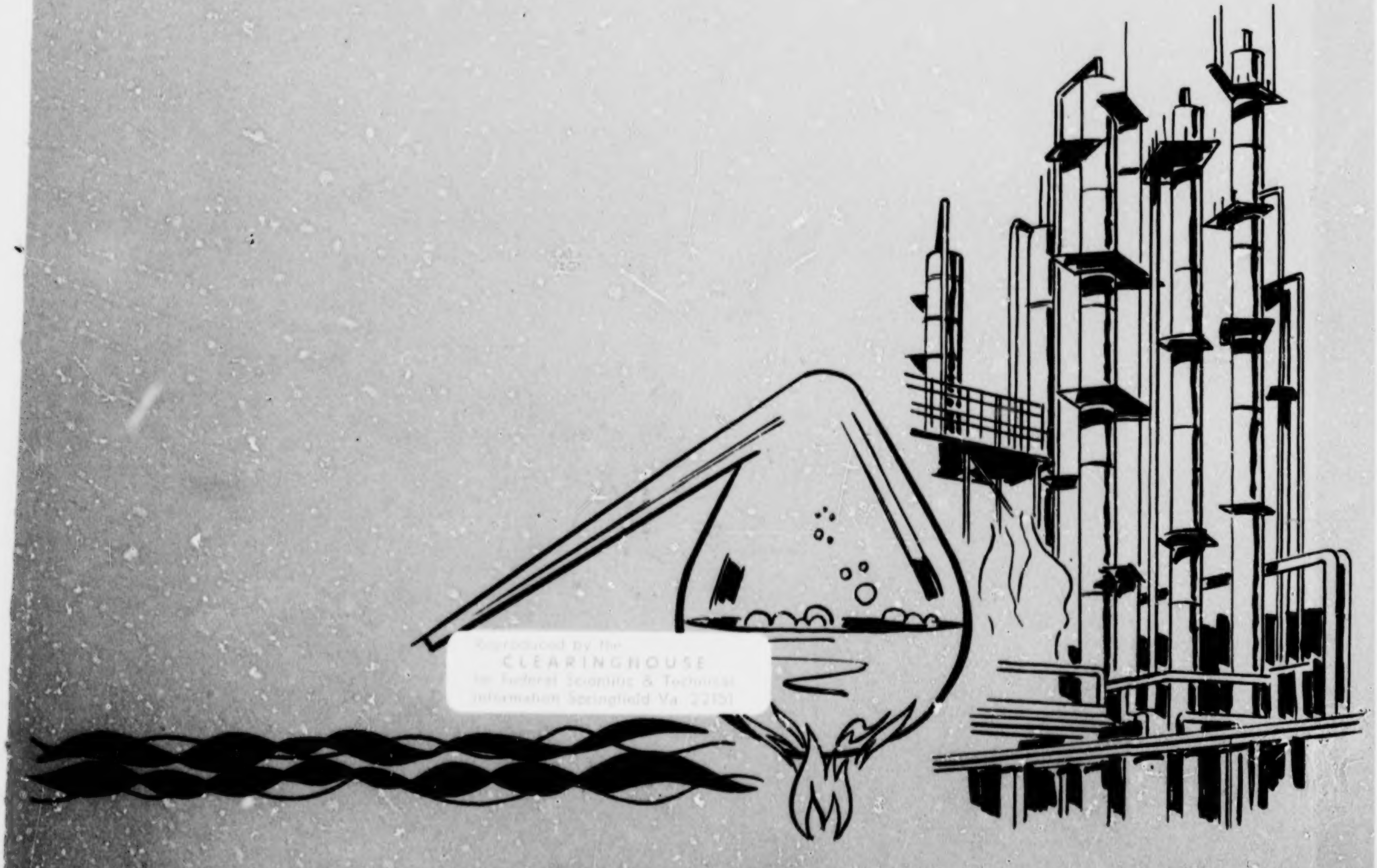
Petrochemical Effluents Treatment Practices

SUMMARY



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THE CHARACTERISTICS AND POLLUTIONAL PROBLEMS ASSOCIATED WITH PETROCHEMICAL WASTES

Summary Report

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RESEARCH NEEDS - CONCLUSIONS AND RECOMMENDATIONS

HISTORY OF THE PETROCHEMICAL INDUSTRY

It is concluded that the petrochemical industry will continue to grow and diversify. The chemical and allied products industry is expected to increase from the present 5.5 billion gallons per year to 23 billion gallons per year by the year 2000. The production and sales of organic chemicals are expected to increase from the present production of 135 billion pounds per year to 200 billion pounds per year by the year 1973. The petrochemical industry is projected to increase nine percent per year through 1975. Water use patterns have changed: in 1954 and 1962, respectively, cooling water requirements were 82 percent and 65 percent of the total water use. The industrial growth rates by geographical areas through 1975 will be 25, 15, and 10 percent, respectively, for the Pacific Coast and Alaska areas, Gulf Coast area, and Southeast, Puerto Rico, and Virgin Islands areas.

It is recommended that an updated profile of this industry be made every five years. Particular emphasis should be directed to the water use and reuse patterns for the newer petrochemical processes, advanced methods of waste handling, changes in water quality criteria for updated processes, and changes in industrial growth patterns.

DESCRIPTION OF THE PETROCHEMICAL INDUSTRY

It is concluded that new products will be developed from existing "intermediate" petrochemicals, but also new petroleum-based derivatives will be developed to a greater extent. In 1955, the total petrochemical production constituted 24 percent, by weight, of the total chemical production. It is expected that the percentage will increase to 41 percent by 1970. It is anticipated that ethylene, an important petrochemical intermediate, will double (14 to 25 million metric tons annually) over the 1970-80 decade. Estimates indicate that about 500 new petroleum products are introduced to the market every year.

It is recommended that each of the major processes developed by the industry be studied with the objective of evaluating the trends in plant locations, effects on area-wide water quality, and treatment requirements.

PETROLEUM RAW MATERIALS

It is concluded that there will be no significant changes in petrochemical feedstocks, although the increasing demand for ethylene and butylene has required the petrochemical industry to look for additional sources of base material. Heavy fractions such as fuel oils are finding an increasing market as the source for these two olefins and other primary petrochemicals.

It is recommended that the patterns of feedstock usage be monitored and major changes be evaluated in terms of the water use and water reuse requirements, potential pollution problems, and product development.

PETROCHEMICAL PROCESSES

It is concluded that the main contribution to environmental pollution from the petrochemical industry at present eminates from process waste streams. However, the principal processes and characteristics of their wastewaters are fairly well understood. The ranges of the waste volumes and organic concentrations vary considerably. Within the same process at different plant sites, the pollutant loads may range by more than one order of magnitude. Typically, the reaction efficiency in the petrochemical industry has a wide variation. This efficiency may range from 60 percent to nearly 100 percent. Although the feedstock is recycled in the case of low conversion efficiency, the practice is highly dependent on market conditions. In addition to product losses, there are mechanical losses and waste streams that contain side-products.

It is recommended that comparative cost analyses be made on several typical recycle (feedstock) practices and on associated wastewater treatment requirements, establishing a basis for optimizing the overall plant operations. First, comparative studies need to be made on a computerized model basis where operating variables can be generated and the results studied in detail. Second, a series of field studies should be made to test the model data and demonstrate the interrelationships of product handling with wastewater treatment costs.

CHEMICAL AND PROCESS RELATED CLASSIFICATION OF WASTES

It is concluded that many of the conventional parameters, as compared to those developed for characterizing domestic wastewaters, do not adequately define the potential pollution characteristics of petrochemical wastes. In many cases, the pertinent characteristics of a waste stream were ignored, the analytical procedures were inadequate for such complex wastes, and much of the reported data have been misinterpreted. Significant inconsistencies have been found in the measurement of organic carbon, including oil and oil-like substances; oxygen demand of compounds, as measured both chemically and biochemically; toxicity as reflected in both microbial and higher forms of plant and animal life, including man; interferences between petrochemical process waste constituents and reagents used in conventionally-accepted organic and inorganic characterization analyses; and availability of nutrients.

It is recommended that a comprehensive and coordinated evaluation program be developed specifically for standardizing the characterization techniques of wastewaters containing complex and undefinable petrochemical and related wastewater constituents. Such a program should include a correlation and interpretation of reported data and unpublished but available industrial data. Currently, an evaluation must be made of newly developed analytical techniques in comparison with conventional procedures. Finally, a thorough study must be made on the adaptability of newly developed parameters for governmental and industrial use. The latter study would involve an evaluation of the adaptability of newly developed parameters to (a) uniform nation-wide reporting practices; (b) national monitoring networks; (c) pollution or stream assimilation models (mathematical); and (d) on-stream and continuous monitoring systems.

WASTE POLLUTIONAL EFFECTS AND THEIR CHARACTERIZATION

It is concluded that petrochemical wastes may provide potential pollutants in the form of concentrated oxygen-demanding organic and inorganic materials; organic compounds not amenable to biological degradation; oil and oil-like substances; volatile and nonvolatile suspended materials; color contributing solutions; toxic fractions; compounds responsible for taste and odors; floatables and polymeric products; and agents which interfere with conventional analytical techniques and increasing problems associated with the treatment and/or discharge of heated wastewaters.

Furthermore, it is concluded that much of these wastewaters could be reused within the plants with varying degrees of treatment.

It is recommended that long-term tests be conducted to evaluate the effects of intermediate and product waste streams on (a) aerobic and anaerobic biological degradation rates; (b) toxicity of these wastes on acclimated microbiological cultures, and both micro- and macro-plants and animals; (c) speciation and diversity index evaluations below selected plant sites.

It is further recommended that a serious evaluation be made on the treatment required for in-plant reuse and cost analyses be established on treatment for plant reuse and on treatment for discharge.

It is recommended that a series of studies be initiated to standardize the evaluation of the potential pollutional characteristics of all cooling tower and boiler water preparations, as well as their effects on waste treatment systems.

A detailed evaluation should be made at an early date of all the chemical interferences affecting the BOD and COD tests. Carefully controlled tests should be conducted to establish the BOD_5/BOD_u ratio.

It is additionally recommended that many of the more prevalent petrochemical compounds be analyzed in terms of unit weight of BOD, COD, TOC, and IOD per unit weight of the compound. A similar representation per unit weight of suspended solids discharged from various related processes would be of value.

Special properties of selected waste streams should be studied with respect to fish "tainting" (taste and odors in both finfish and shellfish), induced changes in the surface activity of receiving waters, interaction of waste with chlorine and other water treatment disinfectants, and effects of post polymerization on receiving waters.

Similarly, tests should be conducted to determine the effect of the more common process wastes on benthic organisms, selected plankton, and acclimated biological cultures.

TREATMENT AND CONTROL OF PETROCHEMICAL WASTES

It is concluded that most of the wastewaters produced by the petrochemical industry require some form of primary product recovery and treatment, oil removal, settleable solids removal, and reduction in the organic content. By-product recovery possibilities represent a significant approach in reducing pollutants. There is much room for the use of in-plant separation of product and feedstock for recovery purposes.

It is further concluded that physical separation and disposal schemes have not been used as effectively as possible. For example, combustion processes are often overlooked as a potential disposal process, particularly when the wastes are too concentrated or too toxic for treatment by lower-cost biological methods. Stripping processes can be used more effectively throughout the petrochemical industry to remove volatile fractions from the collection of contaminated stream water runoffs.

Most wastewater from petrochemical plants contain wastes which are amenable to biological degradation. A significant group of these wastes exhibit a low biodegradation rate. Consequently, an optimal balance between physical, chemical, and biological treatment (with process modifications) must be considered in the development of a pollution abatement master plan.

For optimum wastewater management in the petrochemical industry, it is necessary to develop the wastewater treatment as an integral process of the overall plant. This necessitates the development of increased product and feedstock recovery, improved housekeeping, separation of noncontaminated wastes from waste streams, and separation of concentrated nonsoluble or otherwise solid fractions near each source.

Additionally, it is concluded that the master plan for in-plant wastewater collection should include facilities to segregate process waste from less contaminated streams. The latter falls into two categories: (a) those wastes derived from dry weather flows such as leaks from pumps, sample ports, packaging, container washings, kettle or batch operations; and (b) those wastewaters derived from wet weather runoffs. The containment and treatment of certain storm flows need evaluation.

It is recommended that the following treatment and control evaluations be considered:

A. Physical Treatment Processes

1. The problem of oil-water and other emulsions should be studied, both with respect to influences on secondary biological waste treatment and the most efficient methods of breaking the emulsions, thus enhancing separation.

2. As the process streams are reused or recycled, the effluents will become increasingly warmer. Emphasis should be directed to evaluating methods of cooling various waste streams prior to subsequent treatment.

3. Many waste streams contain inorganic and organic solids which are difficult to remove (i.e., lime sludges containing heavy tars, oils, etc.). Physical separation processes in conjunction with coagulant aids, therefore, should be more thoroughly investigated.

B. Chemical Treatment

1. The development of better techniques for evaluating the effects of various cooling tower and boiler water additives on secondary biological treatment and such analyses as may be affected adversely by these additives should be undertaken.

C. Biological Treatment

1. Evaluation of the effect of various wastes on bioflocculation, settling, and all types of biological treatment systems is recommended. Specific attention should be directed to the toxic characteristics of these wastes.

2. The magnitude of biological reaction rates for major process wastes within the petrochemical industry should be established.

3. Biological process modifications to maximize COD reduction should be developed.

4. A determination of the effects of various wastewaters on streams and brackish waters in terms of both biodegradation rates and reaeration rates should be made.

5. A more satisfactory way of evaluating concentrations of pollutants in brackish and salt waters should be developed.

6. The advantages (if any) of two-stage biological treatment versus single-stage biological treatment should be determined. Similarly, the advantages (if any) of tertiary treatment over other disposal means should be investigated.

7. The availability of complexed forms of nitrogen and phosphorus as a nutrient source to microorganisms in biological waste treatment plants should be evaluated.

D. Other Methods of Disposal

1. The technology by which persistent contaminants in benthic deposits can be studied should be developed.

2. Guidelines for the development of dilution thresholds for common petrochemical toxicants with respect to co-treatment with municipal wastes should be established.

ECONOMIC ASPECTS OF PETROCHEMICAL WASTE TREATMENT

It is concluded that most waste streams from petrochemical plants will require some form of solids or oil separation, waste stream separation and pretreatment, and secondary biological treatment. The cost of this wastewater treatment can be reduced considerably by in-plant reuse of product waste streams and wastewater in general. Trends toward the co-treatment and joint treatment of industrial wastewaters necessitate the establishment of a formula for equitably prorating pollution control costs.

It is recommended that a detailed and basic study be initiated to evaluate the cost of treating wastes from single plants or process streams with combined wastes from several plants. The economy of scale in treating petrochemical wastes on an area-wide basis offers many advantages in dampening the effect of peak releases from individual processes, possibly neutralization, utilization and balance of nutrients, and more effective treatment supervision.

However, the economy of scale is subject to geographical limitations. Conveyance costs may override any economy of scale inherent with regional type treatment concepts.

INTRODUCTION

A petroleum chemical industry based on hydrocarbons is relatively new since synthetic chemicals were not produced in significant amounts from petroleum until just prior to World War I. The petroleum industry in the United States developed during 1919 to 1920 as a result of research conducted during World War I. During World War II, the United States produced vast quantities of synthetic rubber which gave the petroleum industry great impetus. Thirty major synthetic rubber, butadiene, and styrene plants were constructed from 1940 to 1950 at a cost of $900 million (16). Following the pattern of synthetic rubber production, the petrochemical industry experienced an accelerated rate of growth, increasing over fivefold from 1945 to 1960. This rapid growth continues today with organic chemicals constituting a major product of the petrochemical industry. Ammonia, sulfur, and carbon black are major inorganic products which are being manufactured in large quantities within the petroleum industry.

There are several reasons for the rapid growth of the petrochemical industry, including the rise of industries which process petrochemicals into final products such as plastics and synthetic fibers; the availability of cheap and abundant supplies of petroleum raw materials; the ease and economics of producing petroleum-based chemicals as compared to production using non-petroleum sources; and the increasing cost and limited supply of non-petroleum raw materials.

The locations of the major petrochemical plants in the United States are shown in Figure 1. The center of petrochemical activity in the United States is situated along the Gulf Coast between New Orleans, Louisiana, and Brownsville, Texas. This region contained approximately 80 percent of the nation's petrochemical production capacity in 1960 (16). The major factors for location of the industry in this area include the availability of sea transport, the fact that 75 percent of the United State's petroleum reserves are located within easy reach of this area, the abundance of fresh water, and the large quantities of cheap fuel (gas).

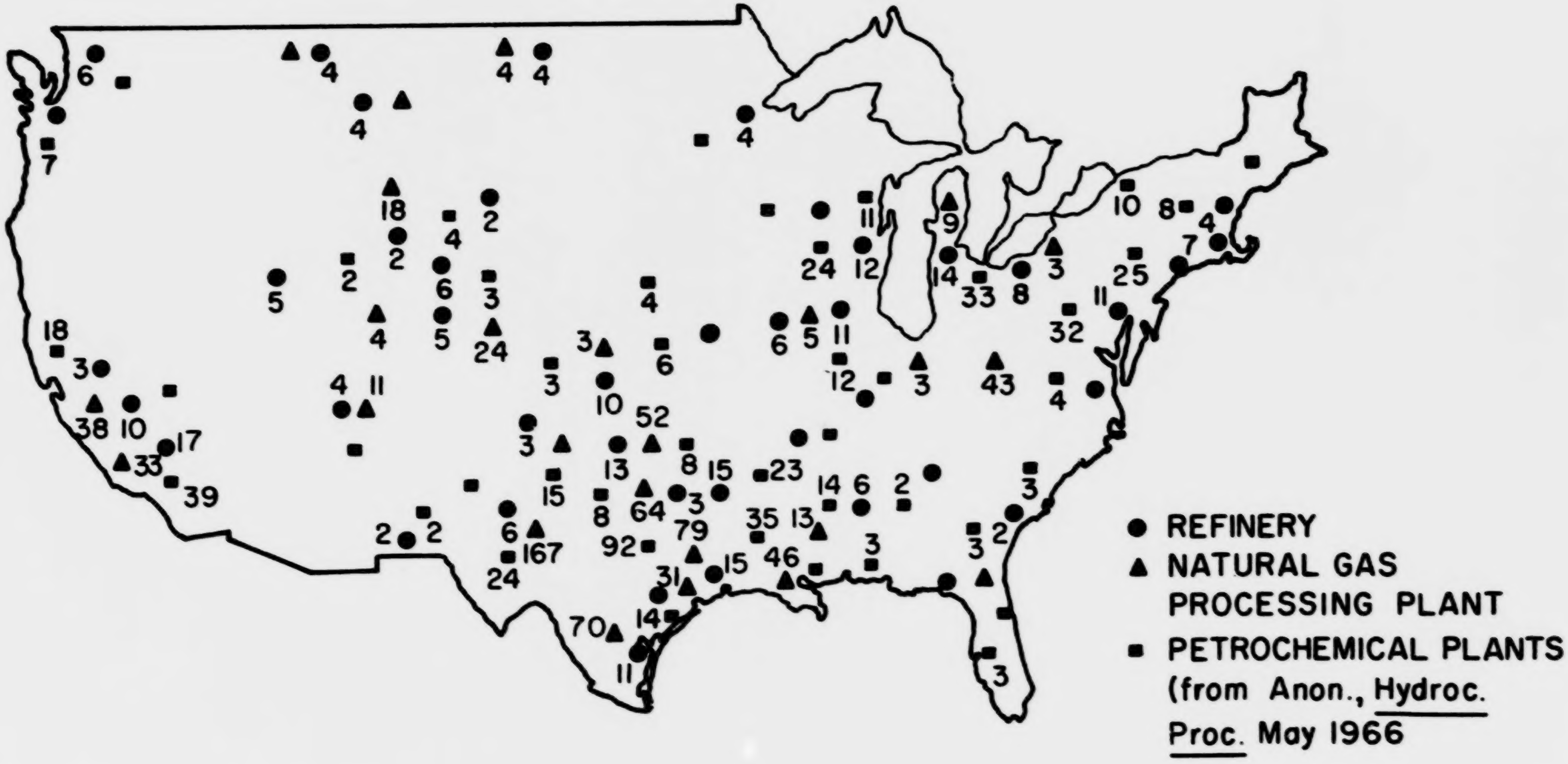
● REFINERY
▲ NATURAL GAS PROCESSING PLANT
■ PETROCHEMICAL PLANTS
(from Anon., Hydroc. Proc. May 1966

FIGURE 1

LOCATION OF HYDROCARBON PROCESSING PLANTS

(Reference Anon., Hydroc. Proc., May 1966)

DESCRIPTION OF THE PETROCHEMICAL INDUSTRY

This description of the petrochemical industry includes raw materials and water requirements, as well as principal products of the industry. Based on this history and description, projections of future petrochemical industrial growth patterns can be made and are included in this section.

WATER USE AND PROJECTION

Although historical water usage data for the petrochemical industry are not separately cited, the 1954 Census of Manufacturers showed that the total chemical and allied products industry used 2,378 billion gallons of water per year. This information was obtained from 1,164 plants which used 20 million gallons or more water per year and comprised 95 percent of the water intake by the industry. Water reuse was practiced by 67 percent of these plants; thus, the gross water usage was 4,032 billion gallons annually. This water's major use was cooling (85 percent), with 9.5 percent employed as process water and the balance utilized for miscellaneous purposes. The water consumed by the chemical industry represented 23.4 percent of the total industrial water use in 1954 (94).

The 1958 Census of Manufacturers reported 933 chemical plants using 20 million gallons or more per year in 1959, resulting in a total water intake of 3,240 billion gallons per year. About 74 percent of these plants employed water reuse, and the gross industrial water use by the chemical industry was 5,225 billion gallons per year. Approximately 66 percent of the total water intake was used for cooling water, a considerable drop from the 83 percent reported in 1954. Process water accounted for 14 percent and water used for the generation of steam and electricity comprised 15 percent of the industry's water intake in 1959. Organic chemical production, which is predominantly petroleum-based, accounted for 44 percent of the annual water intake of the chemical industry.

The latest water use data for the chemical industry were collected in 1962 (14) and included 875 plants in the United States. These data should not be considered to represent the entire chemical industry because some definitions of the industry include packaging, blending, mixing, and distribution of chemical products, most of which use little or no water. The total intake of these plants was 3,600 billion gallons in 1962. The water used for cooling constituted 65 percent of the water intake.

The water intake by the chemical and allied products industries is projected to the year 2000 in Figure 2. Actual water intake for plants which used 20 million or more gallons per year is depicted for 1954 and 1959. The projections indicate that the chemical industry will be the major consumer of industrial water by the year 2000 (94).

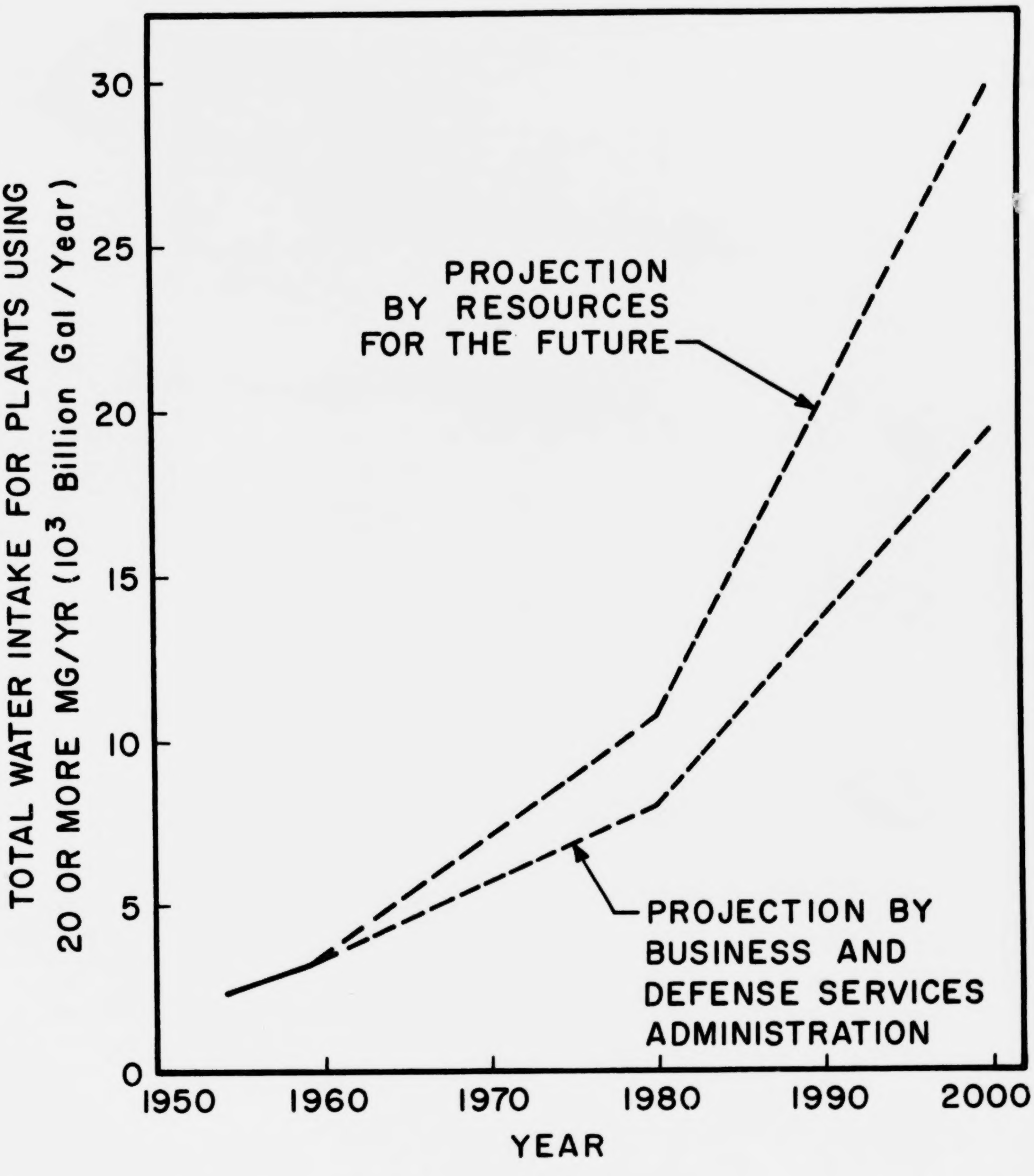

FIGURE 2

TOTAL WATER INTAKE FOR CHEMICAL AND ALLIED PRODUCTS INDUSTRY

PRINCIPAL PRODUCTS AND INTERMEDIATES

"A petrochemical is a chemical compound or element recovered from petroleum or natural gas or derived in whole or in part from petroleum or natural gas hydrocarbons and intended for chemical markets" (119). Most petrochemicals are organic, but a few are inorganic, with the exception of carbon black. Carbon black is a complex chemical which cannot be classified as either completely organic or inorganic, but is still considered as a petrochemical since petroleum is its principal source (96).

The primary or first-generation petrochemicals derived directly from petroleum raw materials are shown in Figure 3. All petrochemical products come from these primary chemicals with the exception of carbon black, which is not further processed. These primary petrochemicals are followed through their intermediate phases to end-products as shown in Figure 4 through Figure 7. Most end-products shown represent raw materials used by subsequent industries in preparing consumer goods.

Examples of major petrochemicals range from ammonia, made from natural gas, to synthetic rubber, which is a mixture of hydrocarbon polymers. This list includes sulfur, carbon black, olefins, polyolefins, olefin derivatives, aromatics and their derivatives, acetylene, phenol, alcohols, ketones, acrylonitrile, acetic anhydride, phthalic anhydride, maleic anhydride, and many others (119).

Relative to primary chemical definition, the olefins comprise the commercial bases for a majority of the synthetic organic chemicals produced in the United States (103). The main chemical processes for the conversion of olefins into chemical derivatives include polymerization, hydration, halogenation, epoxidation, alkylation, and hydrocarboxylation (100).

The aromatics rank second only to olefins in terms of quantities of primary organic petrochemical production. Benzene is the most important of the aromatics in terms of quantity produced.

The paraffins are the least reactive of the hydrocarbons, and all the common processing steps for this family of compounds require elevated temperatures and pressure. The principal paraffinic feedstocks used by the chemical industry are the one-to-five carbon hydrocarbons (96).

Other petrochemicals not categorized herein are also important as product sources. The principal uses of some of these miscellaneous petrochemicals are shown in Figure 7.

PETROLEUM RAW MATERIALS

The first-generation petrochemicals are produced from a variety of petroleum fractions. The four major fractions are natural gas, refinery gas, natural gas condensate, light tops or naphtha, and heavy fractions such as fuel oil.

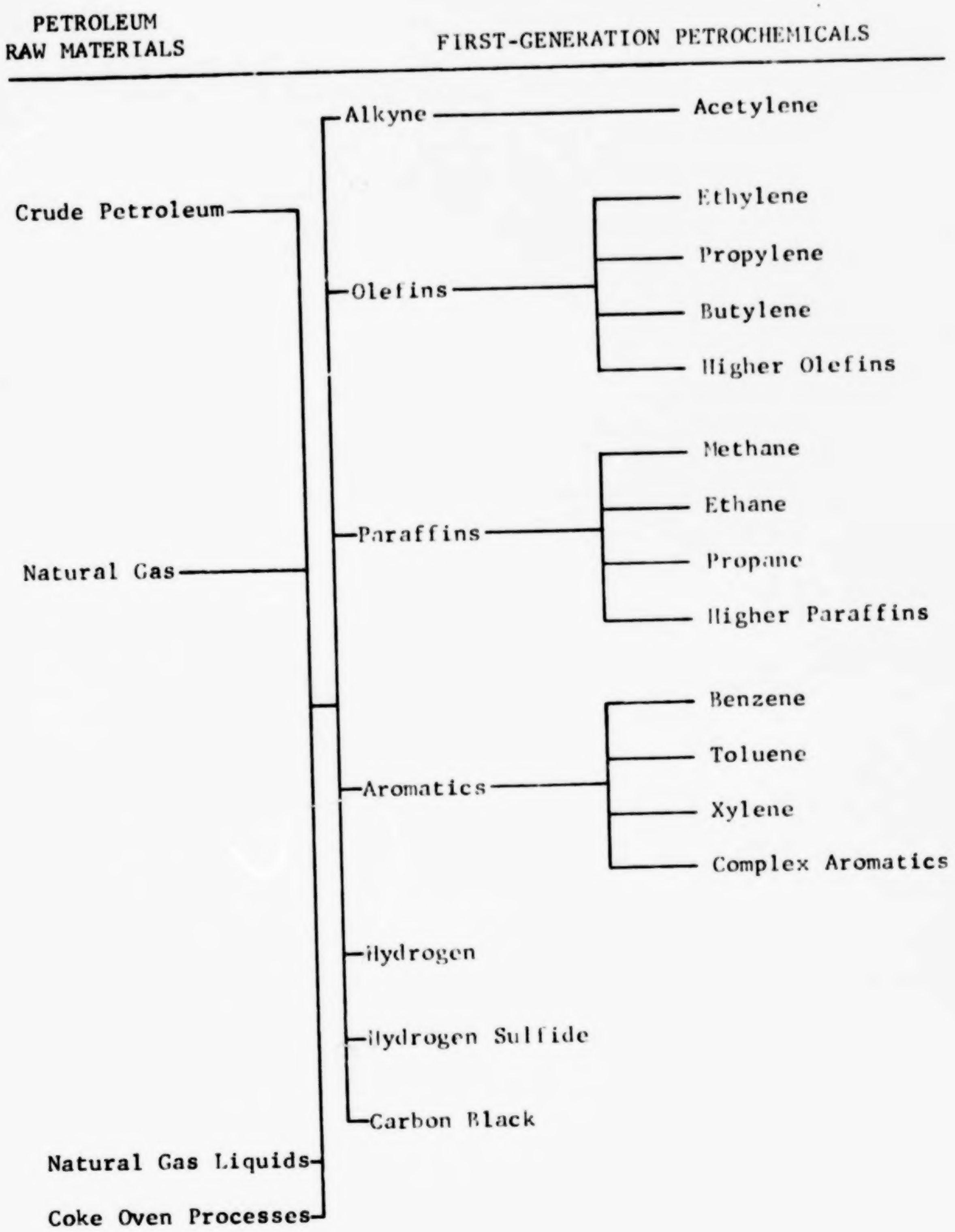

FIGURE 3

FIRST-GENERATION PETROCHEMICALS

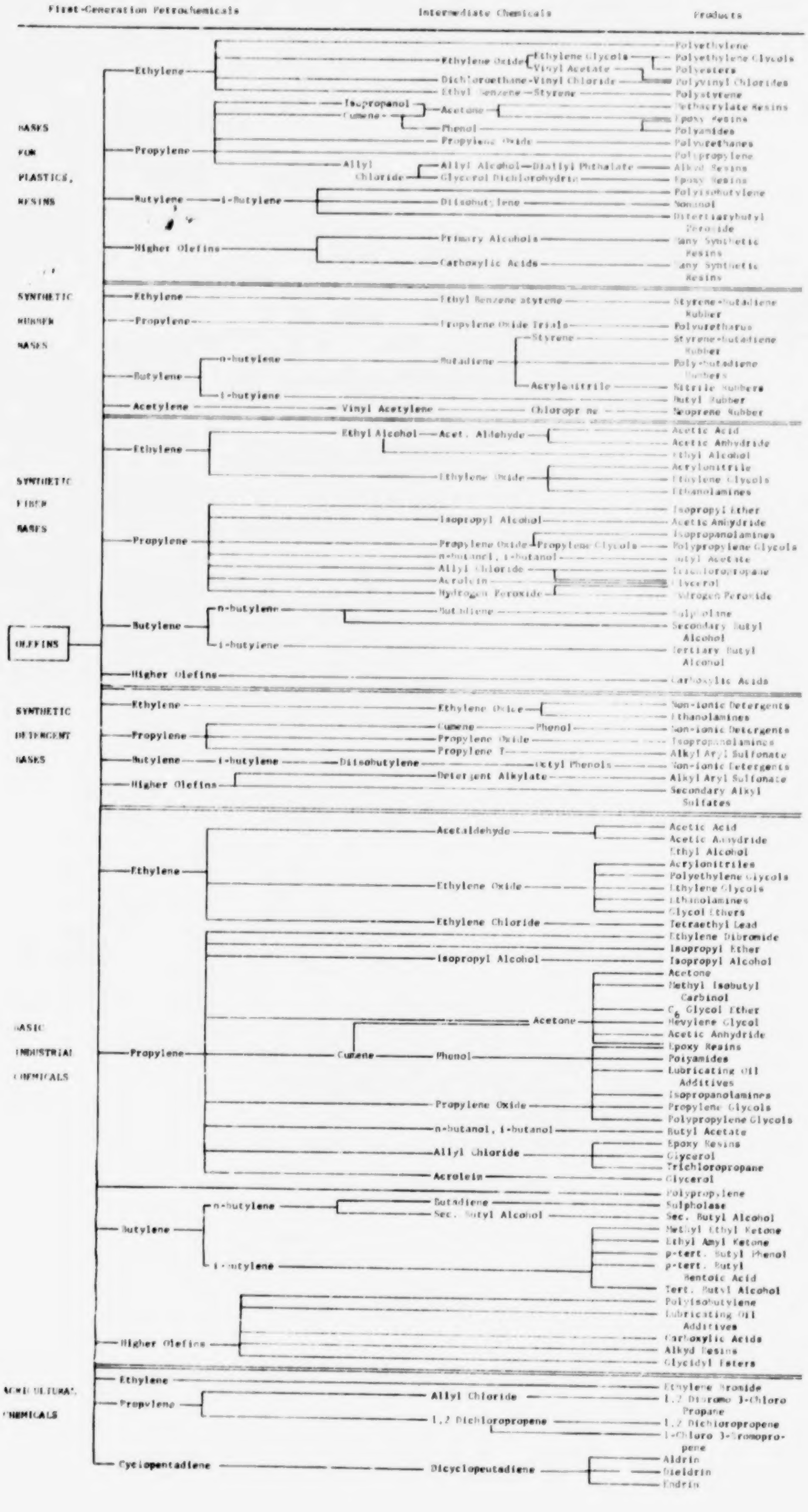

FIGURE 4

PRINCIPAL PRODUCT DERIVATIVES FROM THE OLEFINS

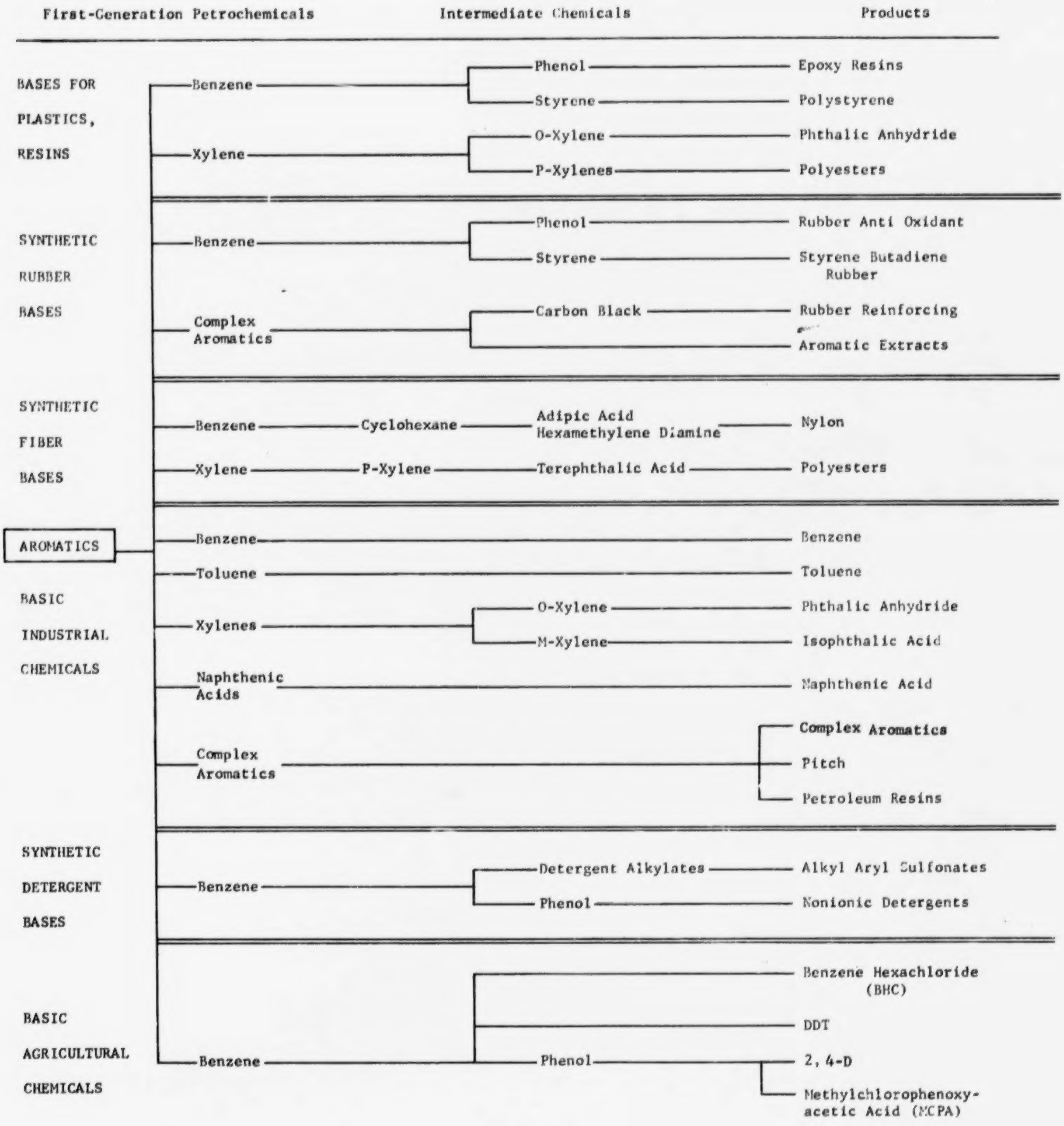

FIGURE 5

PRINCIPAL PRODUCT DERIVATIVES FROM THE AROMATICS

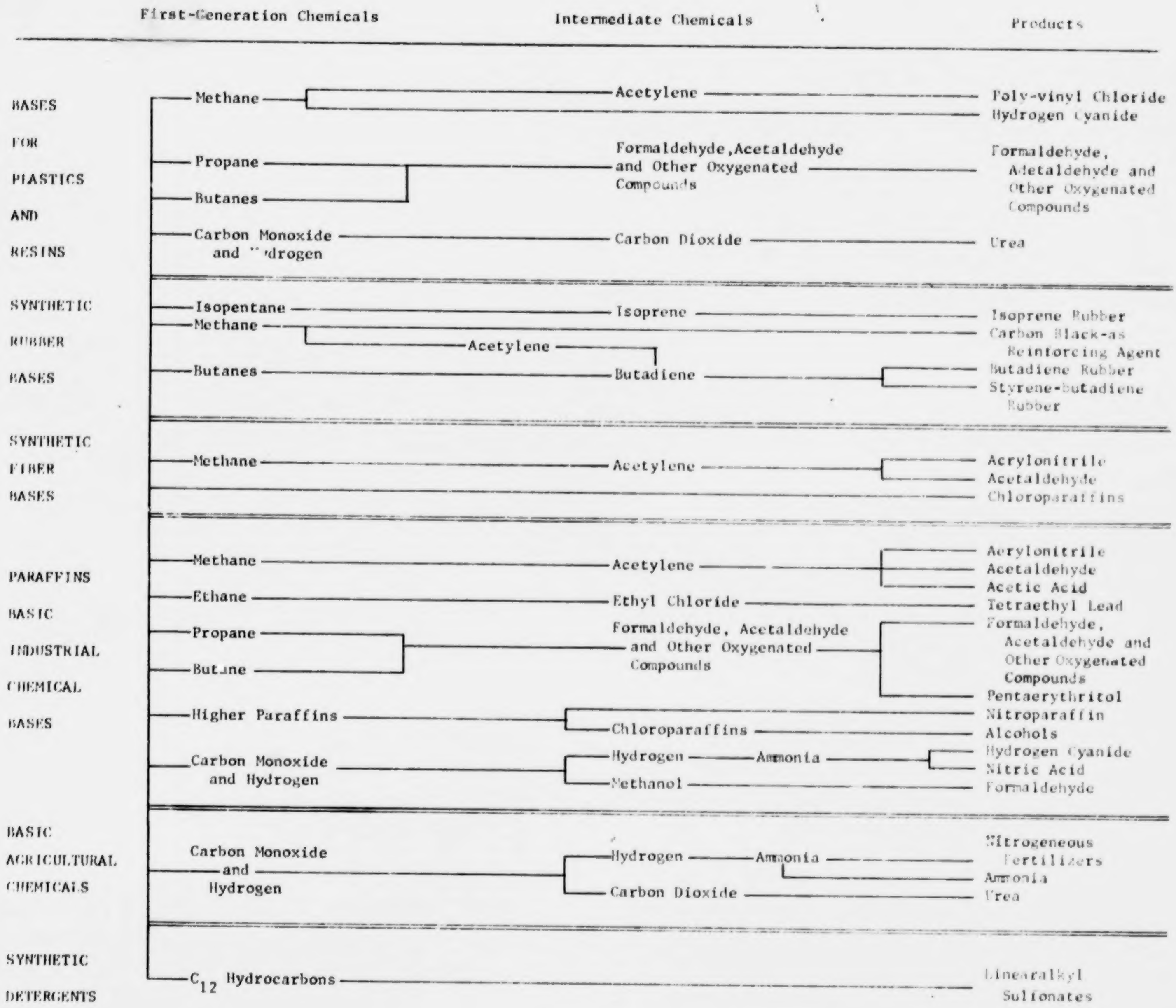

FIGURE 6

PRINCIPAL PRODUCT DERIVATIVES FROM THE PARAFFINS

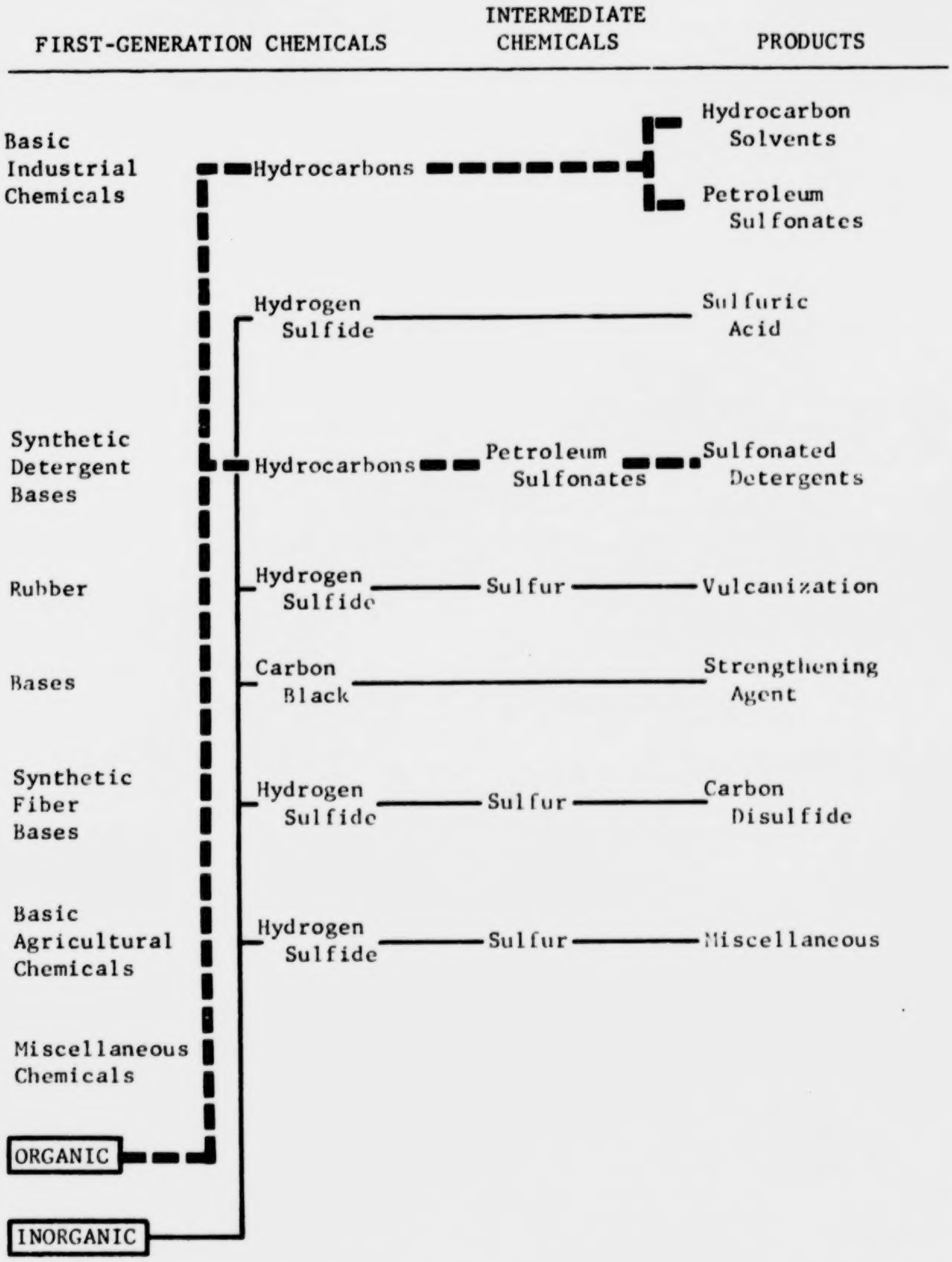

FIGURE 7

PRINCIPAL PRODUCT DERIVATIVES FROM MISCELLANEOUS SOURCES

Natural gas is probably the most desirable chemical feedstock in the United States because it contains a relatively small number of hydrocarbons and because of its availability. Methane is the major constituent of all natural gases with smaller amounts of ethane, propane, butane, and pentane commonly occurring. Small quantities of hydrogen sulfide, nitrogen, and helium may be associated with certain natural gases. Enormous quantities of natural gas are produced in the United States but only about three percent are used for chemical production. The remainder are used for fuel. In the future, larger quantities of natural gas will probably be used in chemical production because of availability and low cost.

Crude petroleum contains a great number of hydrocarbons, most of which are either paraffins, naphthenes, or aromatics. The crude oil is refined by distillation, in order to obtain the fractions used for preparation of the first-generation petrochemicals.

Refinery gases provide an important source of ethylene and propylene used by the petrochemical industry. Once the crude oil has been distilled, the resulting gasoline fractions are further processed by catalytic cracking, which consists of splitting and rearranging hydrocarbon molecules using heat, pressure, and catalysts. Considerable amounts of by-product olefins are formed during cracking operations, and these olefins constitute refinery gas.

Light naphtha contain the lower paraffinic gasoline fractions, which are unsuitable for blending fuels or for conversion to fuel hydrocarbons by catalytic reforming. The fractions generally are converted into olefins and diolefins by cracking in the presence of steam (117).

The heavy fractions such as oils, waxes, and asphalts, which are obtained during the primary distillation of crude petroleum, are finding increasing value as the source of the olefins, ethylene, and butylene. Synthesis gas also can be produced by partially oxidizing the heavy fractions.

PROJECTED GROWTH OF THE PETROCHEMICAL INDUSTRY

The petrochemical industry has experienced tremendous growth and expansion over the last two decades. Estimates of expected growth must be constantly revised to reflect process changes, consumer demands, and feedstocks. The projected data in Table 1 present current estimates of consumption in 1975 for some of the more important petrochemicals.

The outlook for growth in the entire petrochemical industry is favorable. In 1955, petrochemical production comprised about 24 percent by weight of the total chemical production; by 1970, it should account for 41 percent according to this projection (75). Petrochemical sales for 1966 were estimated at $12 billion and, by 1970, are expected to exceed $20 billion (15). The 1966 projection of petrochemical sales for 1970 was about $5 billion higher than a similar projection made in 1961. Petrochemicals should account for 64 percent of the total dollar value of all chemical products by 1970.

TABLE 1

PROJECTION OF UNITED STATES PETROCHEMICAL PRODUCTION CAPACITY FOR SELECTED CHEMICALS

(References 1, 7, 104)

Products and Petrochemical Intermediates	United States Production - billions of pounds/year		
	1954	Recent Data year in parentheses	1975+
Synthetic Fibers			
Acetate	0.34		1.12
Acetic Anhydride	0.696*		2.65*
Nylon	-		0.8-1.0
Polyesters	0.035		1.0
Acrylic Fibers	0.097		1.5-1.6
Acrylonitrile	0.2*		1.5*
Plastics and Resins	2.8	7.74 (1962)	
Phenolic Resins	0.434	0.66 (1962)	1.6*
Phenol	0.6*		2.25*
Formaldehyde	1.03*		7.25*
Phthalic Alkyd and Nonbenzenoid	0.45	0.53 (1962)	1.66
Alkyd Resins			
Phthalic Anhydride	-		-
Synthetic Glycerol	0.115*		0.915*
Styrene Resins	0.481	1.25 (1962)	2.4
Styrene	0.500		2.4
Urea and Melamine Resins	0.265		0.715
Vinyl Resins	0.524	1.55 (1962)	2.5
Polyolefins	-	2.16 (1962)	-
Polyethylene	0.57	4 (1967)	6.93
Polypropylene		0.66 (1967)	2.11
Surface-Active Agents (Not Detergents Themselves)	1.03		1.6
Ethanolamines	0.063		0.153

TABLE 1 (Continued)

PROJECTION OF UNITED STATES PETROCHEMICAL PRODUCTION CAPACITY FOR SELECTED CHEMICALS

Products and Petrochemical Intermediates	United States Production - billions of pounds/year		
	1954	Recent Data year in parentheses	1975+
Synthetic Rubber	1.31		5.6
Copolymer	0.97		4.35
Butyl	0.13		0.4
Neoprene	0.16		0.58
Others	0.052		0.27
Ammonia (from petroleum only)	6.8		11.2
Methanol	1.1		3.6
Methyl Chloride	0.04		0.15
Ethyl Chloride	0.4		1.46
Ethylene Dichloride	0.53		2.1
Ethanol (Synthetic)	1.44		4.9
Ethylene Glycol	0.97		1.6
Ethylene Oxide		15.1 (1967)	21.0
Ethylene			17.3(1971)

+ Estimated Consumption

* Includes Other Uses for Intermediate

Growth of the industry is also evidenced by the number of new projects planned. In 1967, 81 new projects were in the planning or construction stage in the United States, as compared to 41 in 1966 (1). Global capital outlay for new petrochemical facilities was $2.4 billion in 1965 (93). Estimates indicate that approximately 500 new petroleum products are introduced to the market every year (97). In 1966, petrochemical production required the use of 650,000 barrels of petroleum daily, and in 35 years the requirement will be 12 million barrles per day (93).

Plastics and resins, which are primarily used as construction and packaging material, are the most important petrochemical products with respect to volume and projected growth (104). In 1962, 7.7 billion pounds of these materials were produced in the United States with a corresponding domestic consumption exceeding 6.9 billion pounds (97). Polyolefins constitute the most important category in the plastic industry, and by 1975 the world demand for polyolefins is expected to approach 35.2 billion pounds, four times greater than the 1965 global output of these materials (7). Miscellaneous plastics and resins are growing at annual rates of three to four percent.

Synthetic Fibers - World nylon consumption should increase from two billion pounds in 1964 to 3.3 billion pounds by 1975 (96). The United States is expected to provide about 40 percent of the 1975 world nylon capacity. Polyester resins are expected to double in production capacity, and acrylonitrile should increase 165 percent between 1966 and 1975 (15).

Synthetic rubber accounted for 75 percent of total rubber produced in 1966, and this fraction should increase to 82 percent by 1975 with the average annual increase in consumption amounting to about four percent.

Other Petrochemical Products and Intermediates - Nitrogen production on a global basis should rise from 26.5 million tons in 1965 to 50.3 million tons in 1970. In 1967, the United States capacity for ammonia production was 17.3 million tons, an increase of 33 percent over the previous year. Current annual consumption of ethylene is about 14 million metric tons, and this demand is expected to increase by more than 25 million metric tons during the 1970 to 1980 decade.

Effect of New Products on Growth - Based on present projections, the petrochemical industry should continue to grow at least at its present rate. The introduction of new products may even increase the growth rate.

PETROCHEMICAL PROCESSES

A working knowledge of the principal production processes which comprise the major waste sources is necessary for proper evaluation of the complexities associated with petrochemical waste treatment. The petrochemical industry uses many variations of the chemical processes discussed herein, but the details of most of these special processes are proprietary.

PRIMARY CONVERSION PROCESSES

The primary conversion processes constitute what is known as petroleum refining. Four major methods are used to obtain the separation of individual hydrocarbons from crude oil. The flow of the petroleum raw materials through the primary conversion process is schematically shown in Figure 8.

Three types of distillation are used, all involving separation of hydrocarbons by differential boiling characteristics. Distillation at a single pressure level separates compounds on the basis of molecular size, while alternate use of two pressures will separate compounds of different molecular configuration.

The extraction process purifies the mixtures by using solvents which preferentially dissolve defined hydrocarbons. The various hydrocarbons can be separated according to molecular orientation by using selective solvents and different temperatures.

Adsorption and Absorption - Various materials which have selective preference for individual hydrocarbons or impurities can be used in combination or at different temperatures to isolate and purify hydrocarbon mixtures. These materials operate by the mechanisms of adsorption and absorption.

Crystallization - Certain constituents of a mixture can be crystallized from solution by changing the pressure and temperature of the mixture and using specific solvents. The constituent is removed in a purified, solid form.

SECONDARY CONVERSION PROCESSES

Secondary conversion processes are used to convert the purified hydrocarbon feedstocks into the final product exclusive of such final finishing operations as the molding of plastics from polymers and the manufacture of nylon fabrics. The secondary processes and the types of petrochemicals derived from them are presented schematically in Figure 9.

Oxidation is one of the older petrochemical processes, and practically every primary petrochemical feedstock can be involved in an oxidation reaction to obtain usable products. Probably the single most important petrochemical reaction in terms of chemical tonnage produced is the oxidation of ethylene to ethylene oxide.

Chlorination, fluorination, and bromination are all commercially important halogenation reactions. Processes which use the direct addition of a halogen to an olefin are characterized by an absence of by-product formation and a relatively rapid, complete reaction with no side-product formation (112).

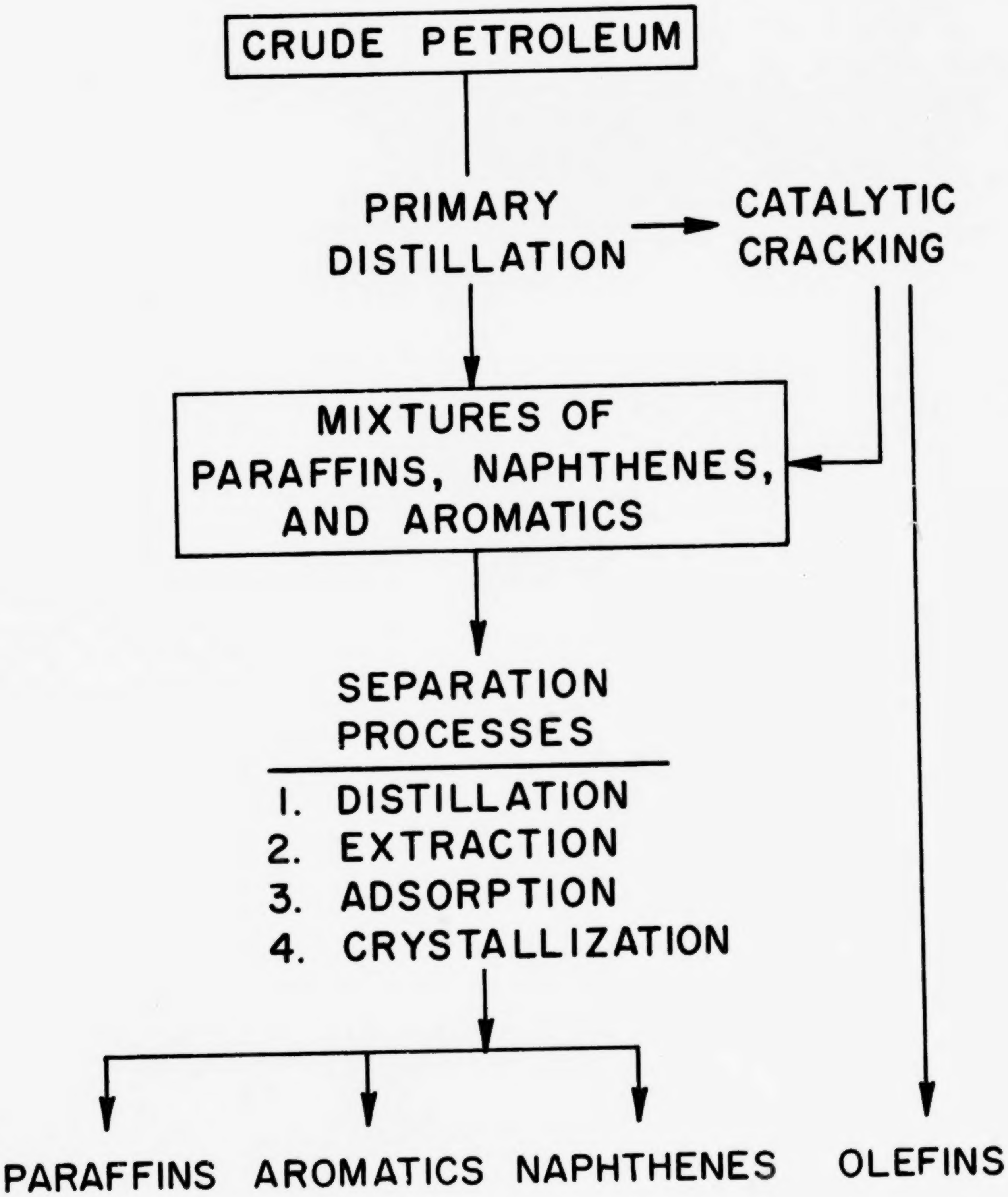

FIGURE 8

PRIMARY CONVERSION PROCESSES

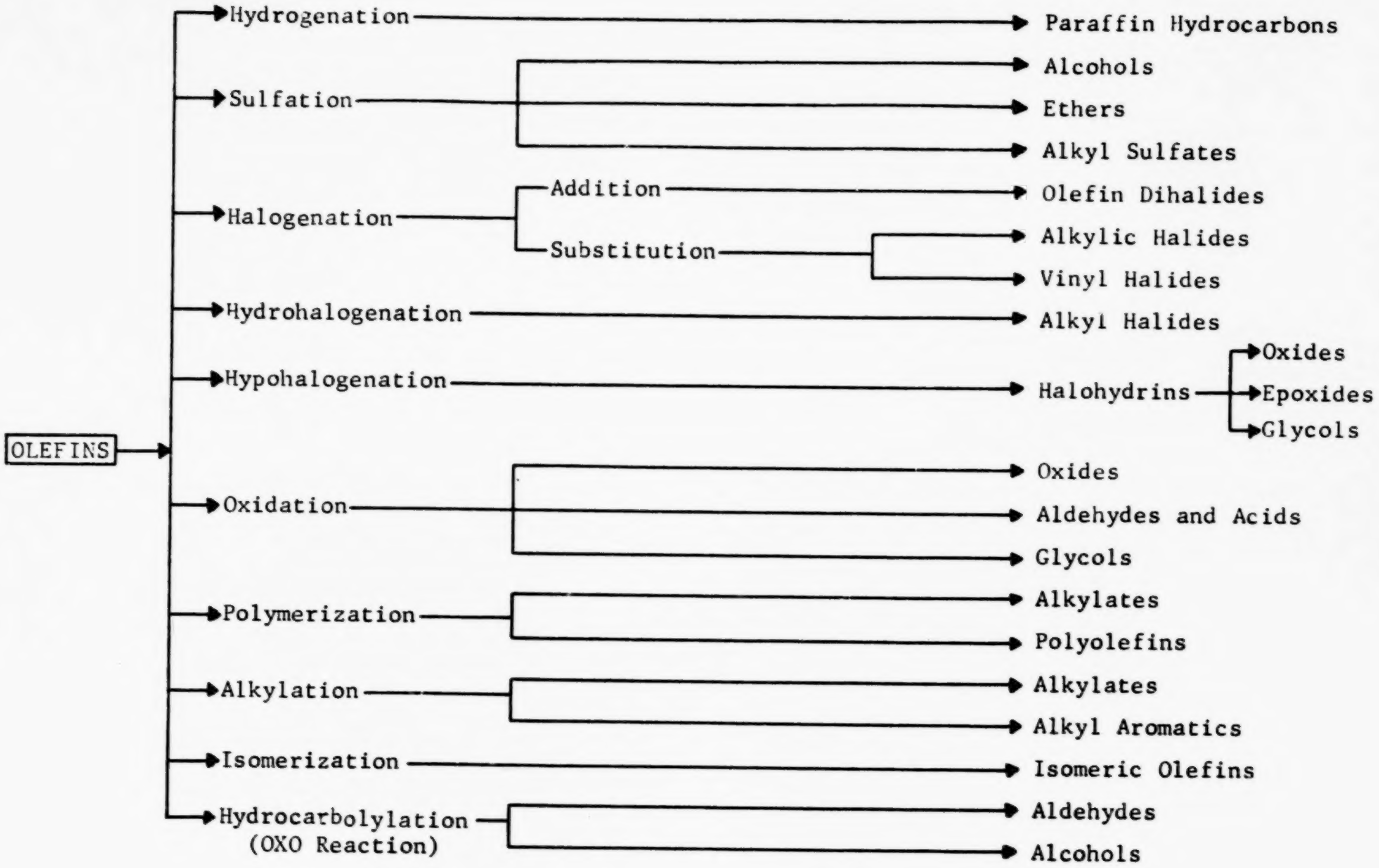

FIGURE 9

SECONDARY CONVERSION PROCESSES

(Reference 52)

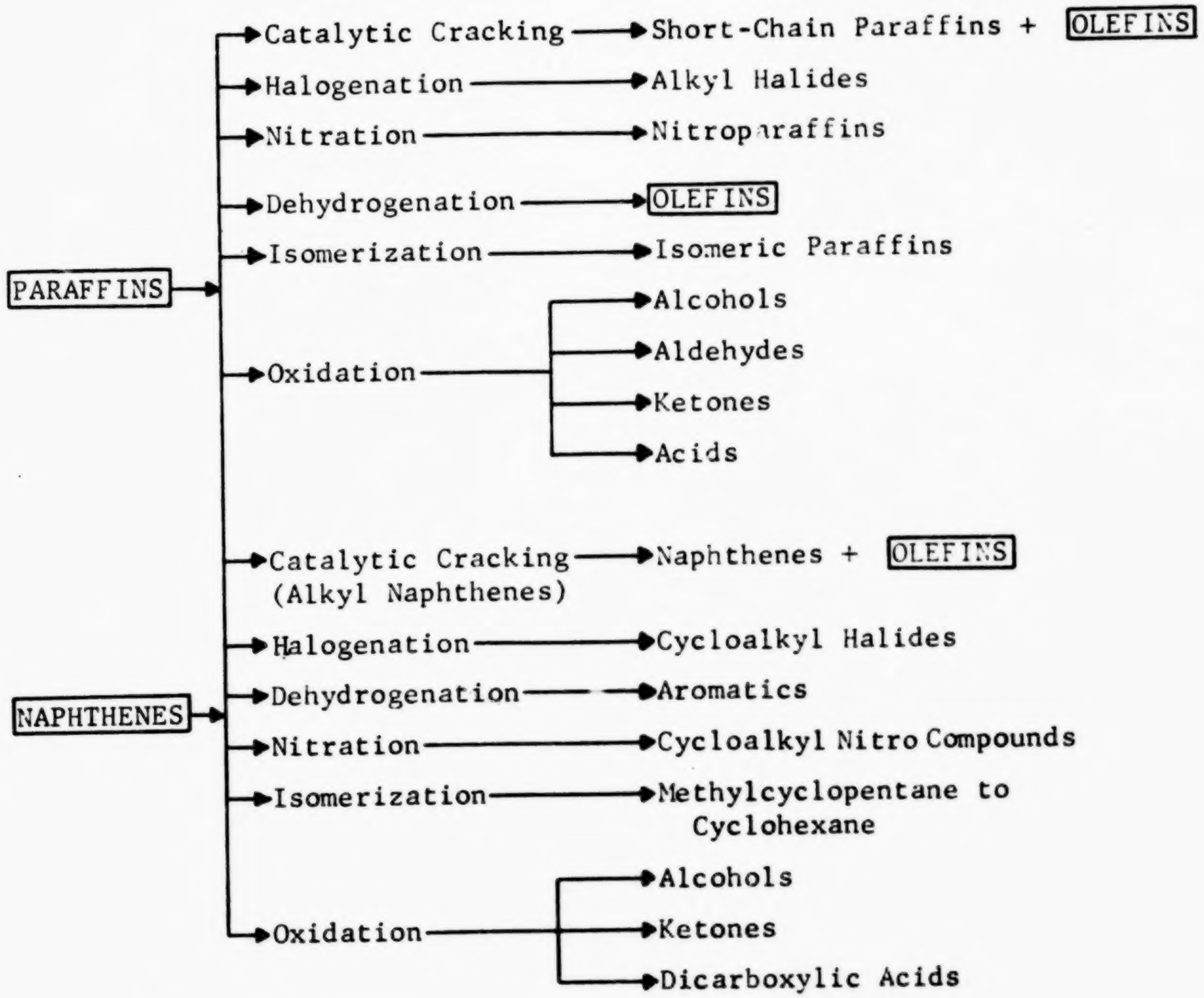

FIGURE 9 (Continued)

SECONDARY CONVERSION PROCESSES

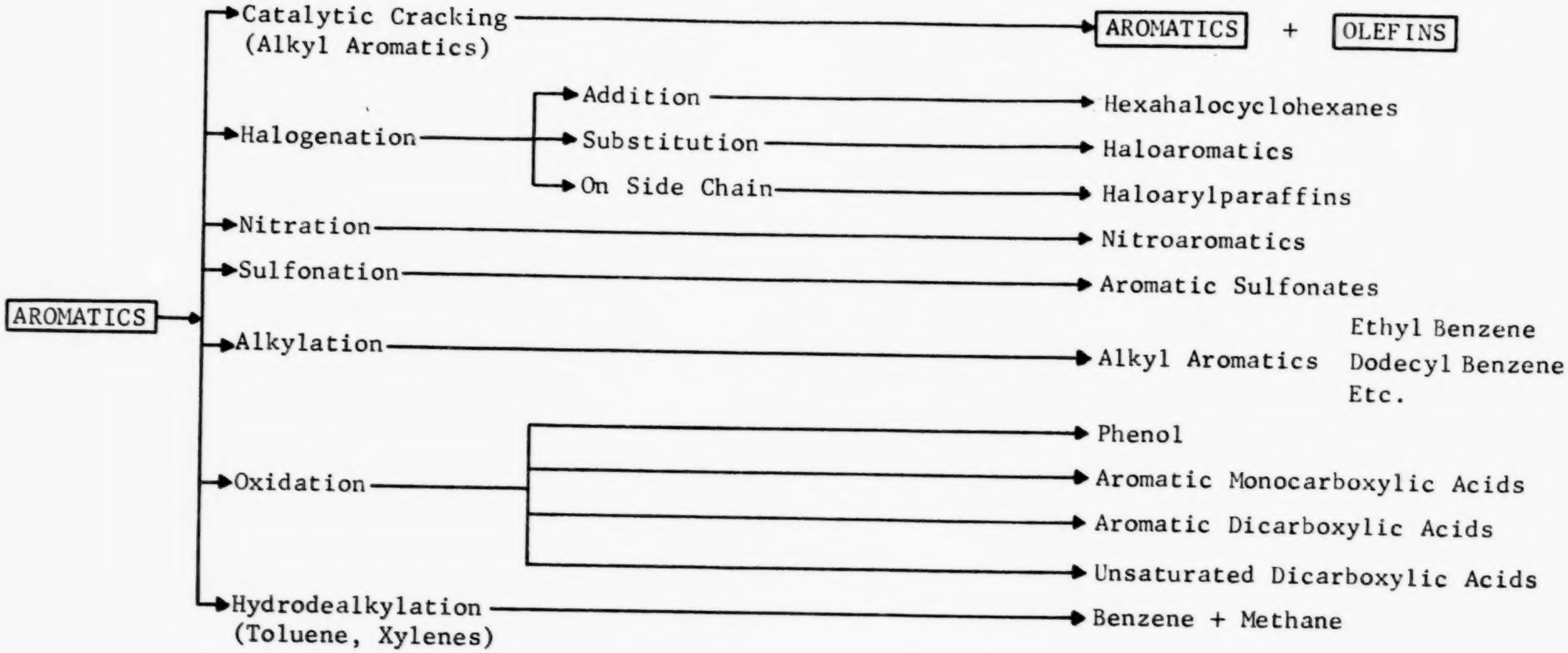

FIGURE 9 (Continued)

SECONDARY CONVERSION PROCESSES

Nitration and Sulfonation - Paraffins and aromatics can both be nitrated; however, the nitrated aromatics have considerably more economic importance than the nitrated paraffins. Nitroparaffins are used primarily as solvents and chemical intermediates. Sulfonation is the addition of the sulfonic acid group ($-SO_3H$) to an organic compound and should not be confused with sulfation, which involves the addition of a sulfate ($-O-SO_3H$) group. Paraffins and aromatics are the hydrocarbons which are most commonly sulfonated in petrochemical production.

The principal alkylation reaction used by the petrochemical industry involves the addition of an olefin to an aromatic compound. The most important of these reactions produce intermediate compounds from benzene, namely, cumene, and dodecylbenzene.

The most significant commercial dehydrogenation process is the formation of butadiene from n-butane and n-butylene. The butadiene process requires the use of catalysts such as iron oxide and alumina-chromium oxide, high reaction temperatures, and reduced pressure. An additional important dehydrogenation use is the dehydrogenation of ethylbenzene to make styrene monomer.

Polymerization processes are best classified in terms of the two mechanisms of polymer formation: step polymerization, a result of the direct interaction of specific functional groups on the monomer; or chain polymerization, which involves the reaction of active centers on the monomers with growth occurring only by the addition of single monomers to the chain. Some of the more common polymerization products include plastics of all types, resins used in adhesives and paints, fibers such as nylon and dacron, and elastomers known as synthetic rubbers.

Other Processes - Ammonia results from the catalytic combination of nitrogen gas and hydrogen gas at high temperature and pressure. The most common catalyst, iron, is used in combination with aluminum and potassium oxides. Hydrocyanation is used to manufacture acrylonitrile, which is used in acrylic fiber and plastics production. Hydrocarboxylation is a process which combines an olefin with carbon monoxide and hydrogen in the presence of a cobalt catalyst to produce aldehydes (52). Sulfation reactions produce alcohols from olefins.

PETROCHEMICAL WASTES

This section presents a brief discussion into the various sources of pollutants which may derive from petrochemical processes. These pollutants are categorized with respect to origin. A chemical classification of petrochemical wastes also is included.

PROCESSES AS WASTE SOURCES

A review of major pollutants in the petrochemical industry reveals that many can be traced to sources common to most petrochemical processes. The characteristics of these sources are listed below (112).

By-products are compounds which result from chemical reaction stoichiometry. In some cases, the by-products formed may have commercial value but often are quite worthless and represent waste disposal problems.

Side-products are formed by reactions competing with primary reactions during petrochemical processing. These side-products are often isomers of the principal product, but they may be reaction products from impurities present in the feedstock. Unlike by-products, side-product formation can often be controlled.

Incomplete Reactions - The product stream from any petrochemical process will contain quantities of unreacted feed. Often in cases of low conversion efficiency the feed chemical is recycled through the process; otherwise, these remaining raw materials are disposed of as wastes.

Every mechanical or physical operation is subject to various losses inherent within the individual operation being performed. Mechanical losses include fluid losses from valves, defective seals in compressors and pumps, leaks in various units, etc. Accidental losses may be attributed to leaks, spills, explosions, as well as poor operation.

WASTE CHARACTERISTICS

Principal pollutional characteristics of petrochemical wastes will be defined in accordance with the unit process from which these wastes are discharged. This characterization will deal primarily with the type of compound present in the process waste stream.

Cooling waters often contain organic contaminants because of pipe leakages which may result in oil contamination and the addition of organic corrosion inhibitors. Recirculated cooling water will tend to concentrate dissolved solids, and the blowdown from such a system may create waste disposal problems. Potential pollutants and other characteristics of typical cooling water operations are shown in Table 2.

Process Effluents - Most of the highly polluted waste streams from a petrochemical plant originate from process areas. This category includes condensed steam from stripping operations, wash waters from process drum cleaning operations, water formed or eliminated during various reactions, and other similar in-process sources. A variety of pollutants are found in these wastewaters, including a portion or all of the feedstock chemicals, products, by-products, side-products, and spent catalytic materials.

TABLE 2

COMPOSITION OF CLEAN WATER EFFLUENT

(Reference 88)

Water Sources	Total Waste-water (%)	Flow Range (gpm)	Sources	Potential Pollutants	
				Type	Concentration Range (mg/1)
Cooling Water (excluding sea water)	40-80	100-10,000 (500-200,000 gal. water ton product)	Process Leaks: Bearings, Exchangers, Etc.	Extractables	1-1,000
				Mercaptans	
				Sulfides	
				Phenols	0-1,000,but usually less than 1 ppm
				Cyanide	
				Misc. N compounds	
				Acids	
			Water Treatment	Chromate	0-60
				Phosphate	0-60
				Heavy metals	0-30
				Fluoride	0-10
				Sulfate	100-10,000
				Biocides, algicides	0-50
				Misc. organics	0-100
			Scrubbed from Air through Tower	Hydrogen sulfide	
				Sulfur dioxide	0-1,000
				Oxides of nitrogen	
				Ammonia	
				Particulates	0-300
			Make-up Water	Total dissolved solids	100-5,000

TABLE 2 (Continued)

COMPOSITION OF CLEAN WATER EFFLUENT

Water Sources	Total Waste-water (%)	Flow Range (gpm)	Sources	Potential Pollutants	
				Type	Concentration Range (mg/1)
Cooling Water (cont.)				Particulates	0-100
				Phosphates	0-5
				Fluoride	0-2
Steam Equipment	10	50-1,000	Boiler Blowdown	Total dissolved solids	500-10,000
				Particulates	5-300
				Extractables	0-10
				Phosphate	1-50
				Sulfite	0-50
				Sulfide	0-5
				Misc. Organic compounds	0-200
				Misc. N compounds	1-100
				Heavy metals	0-10
				Alkalinity	50-400
			Waste Condensate	Extractables	0-100
				Ammonia	0-10

Solvent processes are used in petroleum processing to purify the various chemical feedstock, intermediates, and products. In most instances, the solvents used by the industry are expensive and are recovered to a large extent. However, waste streams from the processes using solvents commonly contain quantities of these materials.

Caustic washes utilizing aqueous sodium hydroxide solutions are frequently used in petrochemical processes. Sodium hydroxide solutions are used to extract from the process stream acidic contaminants such as hydrogen sulfide, mercaptans, phenols, thiophenols, and organic acids (20). Most spent caustic streams, therefore, can be expected to contain quantities of these compounds in the form of sodium salts and unreacted sodium hydroxide, as well as small amounts of the process products and feed chemicals.

Acidic Washes - Petrochemical processing employs acidic washes to remove basic materials from process streams. Acid washes are also used in removing contaminants from phenolic product streams and other process waters. Phenolic spent caustics are neutralized with acids or flue gases to produce an acidic oily stream referred to as "spring acid."

Washing and Scrubbing Procedures - Caustic and acid washings are often followed by clear water rinses to remove all traces of the washing compounds. Water is used also to scrub off contaminant gases from various units. The waste streams from these washing and scrubbing operations contain pollutants which are similar in nature but lower in concentration to those found in the spent caustic and acid washes.

Crude Petroleum Desalting - The desalting of crude oil is a petroleum refinery process and, thus, found only in petrochemical plants which include primary processing of crude oil feedstocks. Crude petroleum desalting produces an effluent stream with a very high salt concentration, considerable oils, a rather high oxygen demand, and other contaminants such as abrasive sediments, and vanadium organometal compounds (20).

Typical processes and resulting pollutants are presented in Table 3. Some selected materials along with their common wastewater characteristics are shown in Table 4. Statistical plots of the more common parameters of flow, BOD, and COD are presented in Figure 10.

CHEMICAL CLASSIFICATION OF PETROCHEMICAL WASTES

The vast number of products manufactured by the petrochemical industry makes a complete listing of every compound which may be present in a waste stream impractical. The two general classifications, inorganic and organic, have been subdivided as required and are shown in Figures 11 and 12.

TABLE 3

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Alkylation: Ethylbenzene		Tar, Hydrochloric Acid, Caustic Soda, Fuel Oil
Ammonia Production	Demineralization	Acids,Bases
	Regeneration,Process Condensates	Ammonia
	Furnace Effluents	Carbon Dioxide, Carbon Monoxide
Aromatics Recovery	Extract Water	Aromatic Hydrocarbons
	Solvent Purification	Solvents - Sulfur Dioxide, Diethylene Glycol
Catalytic Cracking	Catalyst Regeneration	Spent Catalyst, Catalyst Fines (Silica,Alumina Hydrocarbons, Carbon Monoxide, Nitrogen Oxides)
	Reactor Effluents and Condensates	Acids, Phenolic Compounds, Hydrogen Sulfide Soluble Hydrocarbons, Sulfur Oxides, Cyanides
Catalytic Reforming	Condensates	Catalyst (particularly Pt, Mo), Aromatic Hydrocarbons, Hydrogen Sulfide, Ammonia
Crude Processing	Crude Washing	Inorganic Salts, Oils, Water Soluble Hydrocarbons
	Primary Distillation	Hydrocarbons, Tars, Ammonia, Acids, Hydrogen Sulfide
Cyanide Production	Water Slops	Hydrogen Cyanide, Unreacted Soluble Hydrocarbons

TABLE 3 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Dehydrogenation Butadiene Prod. from n-Butane and Butylene	Quench Waters	Residue Gas, Tars, Oils, Soluble Hydrocarbons
Ketone Production	Distillation Slops	Hydrocarbon Polymers, Chlorinated Hydrocarbons, Glycerol, Sodium Chloride
Styrene from Ethylbenzene	Catalyst	Spent Catalyst (Fe, Mg, K, Cu, Cr, Zn)
	Condensates from Spray Tower	Aromatic Hydrocarbons, including Styrene, Ethyl Benzene, and Toluene, Tars
Desulfurization		Hydrogen Sulfide, Mercaptans
Extraction and Purification Isobutylene	Acid and Caustic Wastes	Sulfuric Acid, C_4 Hydrocarbon, Caustic Soda
Butylene	Solvent and Caustic Wash	Acetone, Oils, C_4 Hydrocarbon, Caustic Soda, Sulfuric Acid
Styrene	Still Bottoms	Heavy Tars
Butadiene Absorption	Solvent	Cuprous Ammonium Acetate, C_4 Hydrocarbons, Oils
Extractive Distillation	Solvent	Furfural, C_4 Hydrocarbons
Halogenation (Principally Chlorination) Addition to Olefins	Separator	Spent Caustic
Substitution	HCl Absorber, Scrubber	Chlorine, Hydrogen Chloride, Spent Caustic, Hydrocarbon Isomers and Chlorinated Products, Oils

TABLE 3 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
	Dehydrohalogenation	Dilute Salt Solution
Hypochlorination	Hydrolysis	Calcium Chloride, Soluble Organics, Tars
Hydrochlorination	Surge Tank	Tars, Spent Catalyst, Alkyl Halides
Hydrocarboxylation (OXO Process)	Still Slops	Soluble Hydrocarbons, Aldehydes
Hydrocyanation (for Acrylonitrile, Adipic Acid, etc.)	Process Effluents	Cyanides, Organic and Inorganic
Isomerization in General	Process Wastes	Hydrocarbons; Aliphatic, Aromatic, and Derivative Tars
Nitration		
Paraffins		By-Product Aldehydes, Ketones, Acids, Alcohols, Olefins, Carbon Dioxide
Aromatics		Sulfuric Acid, Nitric Acid, Aromatics
Oxidation		
Ethylene Oxide and Glycol Manufacture	Process Slops	Calcium Chloride, Spent Lime, Hydrocarbon Polymers, Ethylene Oxide, Glycols, Dichloride
Aldehydes, Alcohols, and Acids from Hydrocarbons	Process Slops	Acetone, Formaldehyde, Acetaldehyde, Methanol, Higher Alcohols, Organic Acids

TABLE 3 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Acids and Anhydrides from Aromatic Oxidation	Condensates Still Slops	Anhydrides, Aromatics, Acids Pitch
Phenol and Acetone from Aromatic Oxidation	Decanter	Formic Acid, Hydrocarbons
Carbon Black Manufacture	Cooling, Quenching	Carbon Black, Particulates, Dissolved Solids
Polymerization, Alkylation	Catalysts	Spent Acid Catalysts (Phosphoric Acid), Aluminum Chloride
Polymerization (Polyethylene)	Catalysts	Chromium, Nickel, Cobalt, Molybdenum
Butyl Rubber	Process Wastes	Scrap Butyl, Oil, Light Hydrocarbons
Copolymer Rubber	Process Wastes	Butadiene, Styrene Serum, Softener Sludge
Nylon 66	Process Wastes	Cyclohexane Oxidation Products, Succinic Acid, Adipic Acid, Glutaric Acid, Hexamethylene, Diamine, Adiponitrile, Acetone, Methyl Ethyl Ketone
Sulfation of Olefins		Alcohols, Polymerized Hydrocarbons, Sodium Sulfate, Ethers
Sulfonation of Aromatics	Caustic Wash	Spent Caustic

TABLE 3 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Thermal Cracking for Olefin Production (including Fractionation and Purification)	Furnace Effluent and Caustic Treating	Acids, Hydrogen Sulfide, Mercaptans, Soluble Hydrocarbons, Polymerization Products, Spent Caustic, Phenolic Compounds, Residue Gases, Tars and Heavy Oils
Utilities	Boiler Blow-down	Phosphates, Lignins, Heat, Total Dissolved Solids, Tannins
	Cooling System Blow-down	Chromates, Phosphates, Algicides, Heat
	Water Treatment	Calcium and Magnesium Chlorides, Sulfates, Carbonates

TABLE 4

WASTEWATER CHARACTERISTICS ASSOCIATED WITH SOME CHEMICAL PRODUCTS

(Reference 88)

Chemical Product	Flow (gal/ton)	BOD (mg/1)	COD (mg/1)	Other Characteristics
Primary Petrochemicals:				
Ethylene	50-1,500	100-1,000	500-3,000	phenol, pH, oil
Propylene	100-2,000	100-1,000	500-3,000	phenol, pH
Primary Intermediates:				
Toluene	300-3,000	300-2,500	1,000-5,000	
Xylene	200-3,000	500-4,000	1,000-8,000	
Ammonia	300-3,000	25-100	50-250	oil, nitrogen,pH
Methanol	300-3,000	300-1,000	500-2,000	oil
Ethanol	300-4,000	300-3,000	1,000-4,000	oil, solids
Butanol	200-2,000	500-4,000	1,000-8,000	heavy metals
Ethyl Benzene	300-3,000	500-3,000	1,000-7,000	heavy metals
Chlorinated Hydrocarbons	50-1,000	50-150	100-500	pH, oil, solids
Secondary Intermediates:				
Phenol, Cumene	500-2,500	1,200-10,000	2,000-15,000	phenol, solids
Acetone	500-1,500	1,000-5,000	2,000-10,000	
Glycerin, Glycols	1,000-5,000	500-3,500	1,000-7,000	
Urea	100-2,000	50-300	100-500	

TABLE 4 (Continued)

WASTEWATER CHARACTERISTICS ASSOCIATED WITH SOME CHEMICAL PRODUCTS

Chemical Product	Flow (gal/ton)	BOD (mg/1)	COD (mg/1)	Other Characteristics
Acetic Anhydride	1,000-8,000	300-5,000	500-8,000	pH
Terephthalic Acid	1,000-3,000	1,000-3,000	2,000-4,000	heavy metals
Acrylates	1,000-3,000	500-5,000	2,000-15,000	solids, color, cyanide
Acrylonitrile	1,000-10,000	200-700	500-1,500	color, cyanide, pH
Butadiene	100-2,000	25-200	100-400	oil, solids
Styrene	1,000-10,000	300-3,000	1,000-6,000	
Vinyl Chloride	10-200	200-2,000	500-5,000	
Primary Polymers:				
Polyethylene	400-1,600		200-4,000	solids
Polypropylene	400-1,600		200-4,000	deashing solvents
Polystyrene	500-1,000		1,000-3,000	solids
Polyvinyl Chloride	1,500-3,000	50-500	1,000-2,000	
Cellulose Acetate	10-200	500-2,000	1,000-5,000	
Butyl Rubber	2,000-6,000	800-2,000	2,500-5,000	
Dyes and Pigments:	50,000-250,000	200-400	500-2,000	heavy metals ,color, solids, pH
Miscellaneous Organics:				
Isocyanate	5,000-10,000	1,000-2,500	4,000-8,000	nitrogen
Phenyl Glycine	5,000-10,000	1,000-2,500	4,000-8,000	phenol
Parathion	3,000-8,000	1,500-3,500	3,000-6,000	solids, pH
Tributyl Phosphate	1,000-4,000	500-2,000	1,000-3,000	phosphorus

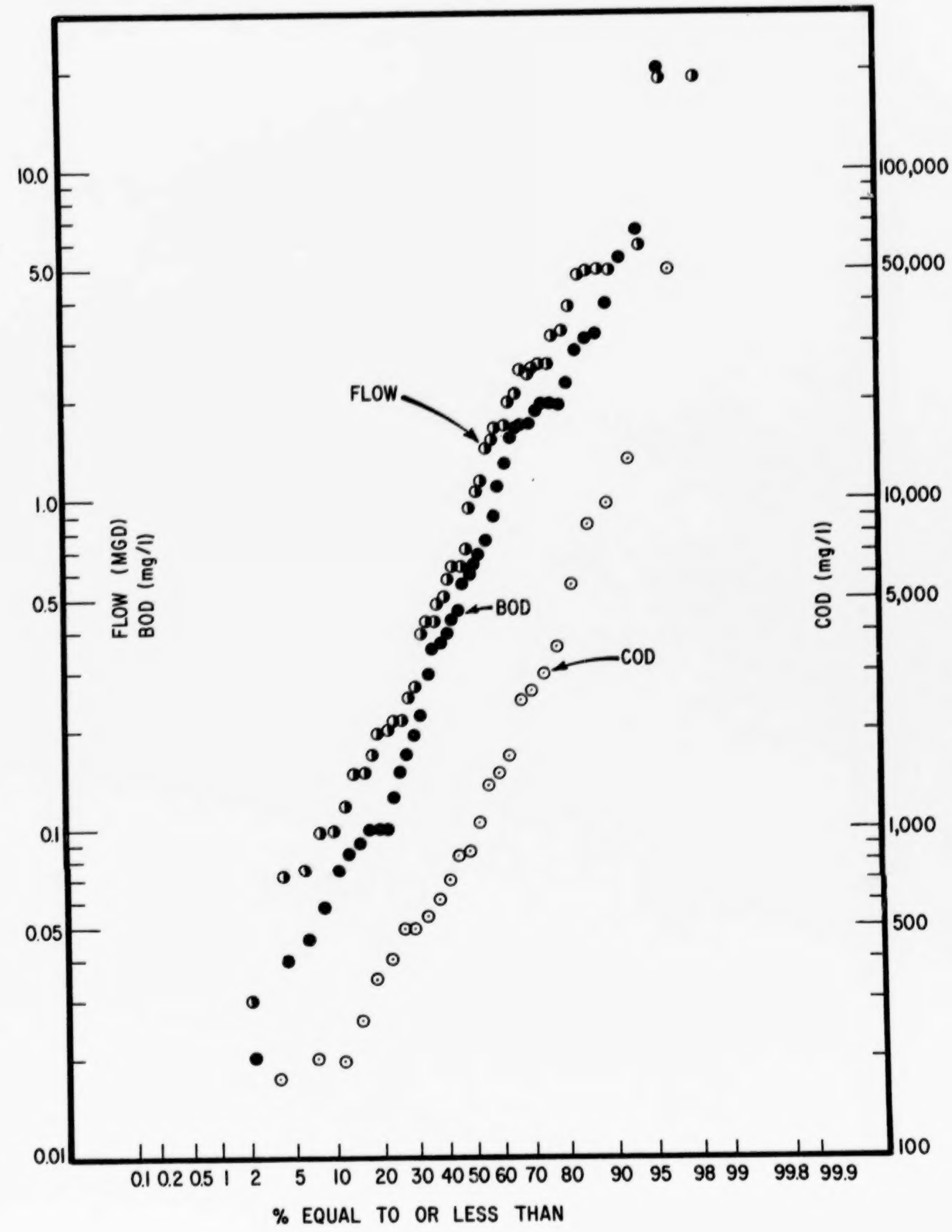

FIGURE 10
PETROCHEMICAL WASTEWATER CHARACTERIZATION: FLOW, BOD, COD

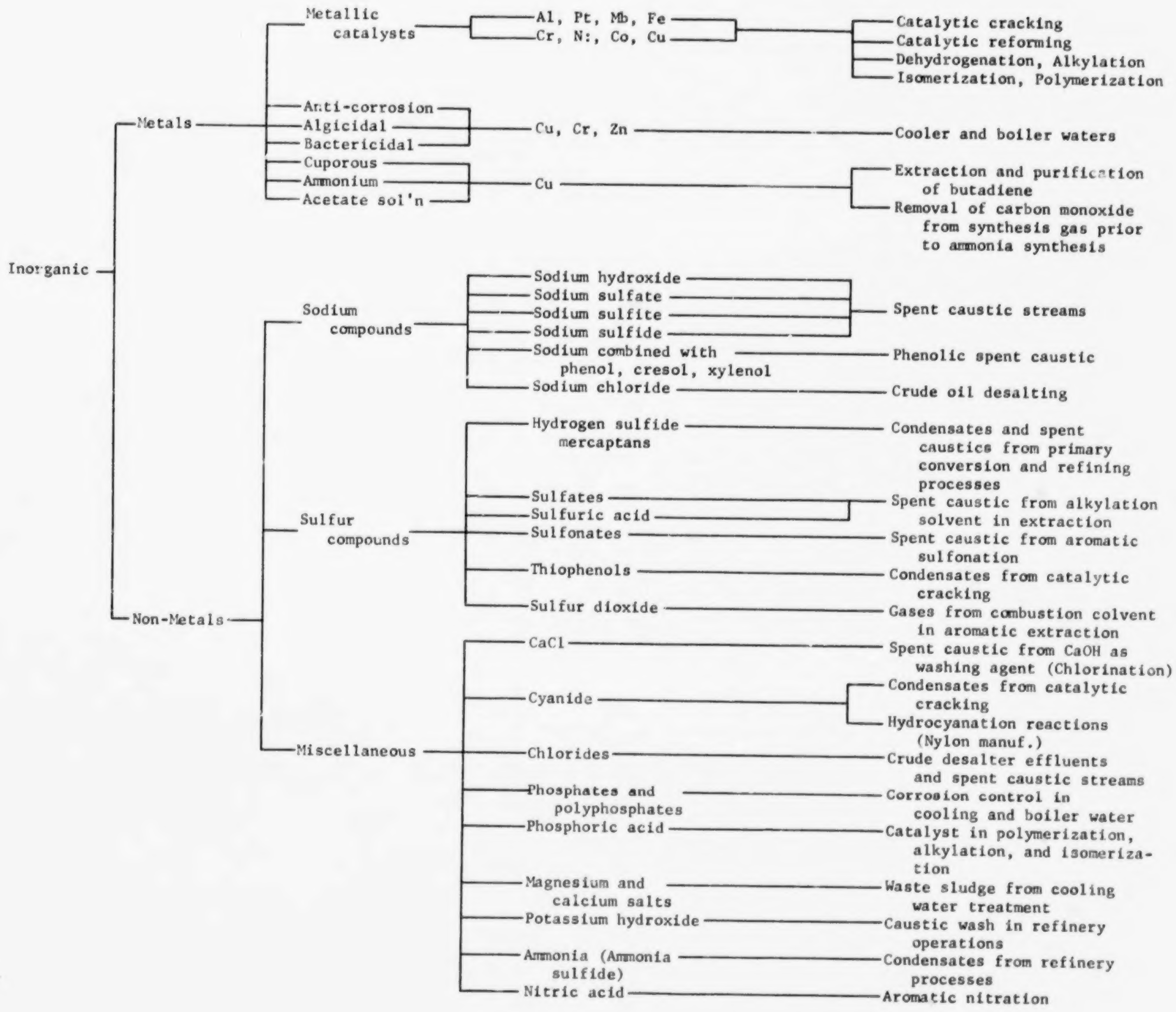
Inorganic
Metals
Metallic catalysts
Al, Pt, Mb, Fe
Cr, Ni, Co, Cu
Catalytic cracking
Catalytic reforming
Dehydrogenation, Alkylation
Isomerization, Polymerization
Anti-corrosion
Algicidal
Bactericidal
Cu, Cr, Zn
Cooler and boiler waters
Cuporous
Ammonium
Acetate sol'n
Cu
Extraction and purification of butadiene
Removal of carbon monoxide from synthesis gas prior to ammonia synthesis
Non-Metals
Sodium compounds
Sodium hydroxide
Sodium sulfate
Sodium sulfite
Sodium sulfide
Spent caustic streams
Sodium combined with phenol, cresol, xylenol
Phenolic spent caustic
Sodium chloride
Crude oil desalting
Sulfur compounds
Hydrogen sulfide mercaptans
Condensates and spent caustics from primary conversion and refining processes
Sulfates
Sulfuric acid
Spent caustic from alkylation solvent in extraction
Sulfonates
Spent caustic from aromatic sulfonation
Thiophenols
Condensates from catalytic cracking
Sulfur dioxide
Gases from combustion colvent in aromatic extraction
Miscellaneous
CaCl
Spent caustic from CaOH as washing agent (Chlorination)
Cyanide
Condensates from catalytic cracking
Hydrocyanation reactions (Nylon manuf.)
Chlorides
Crude desalter effluents and spent caustic streams
Phosphates and polyphosphates
Corrosion control in cooling and boiler water
Phosphoric acid
Catalyst in polymerization, alkylation, and isomerization
Magnesium and calcium salts
Waste sludge from cooling water treatment
Potassium hydroxide
Caustic wash in refinery operations
Ammonia (Ammonia sulfide)
Condensates from refinery processes
Nitric acid
Aromatic nitration

FIGURE 11

CLASSIFICATION OF INORGANIC COMPOUNDS WHICH MAY OCCUR IN PETROCHEMICAL WASTESTREAMS

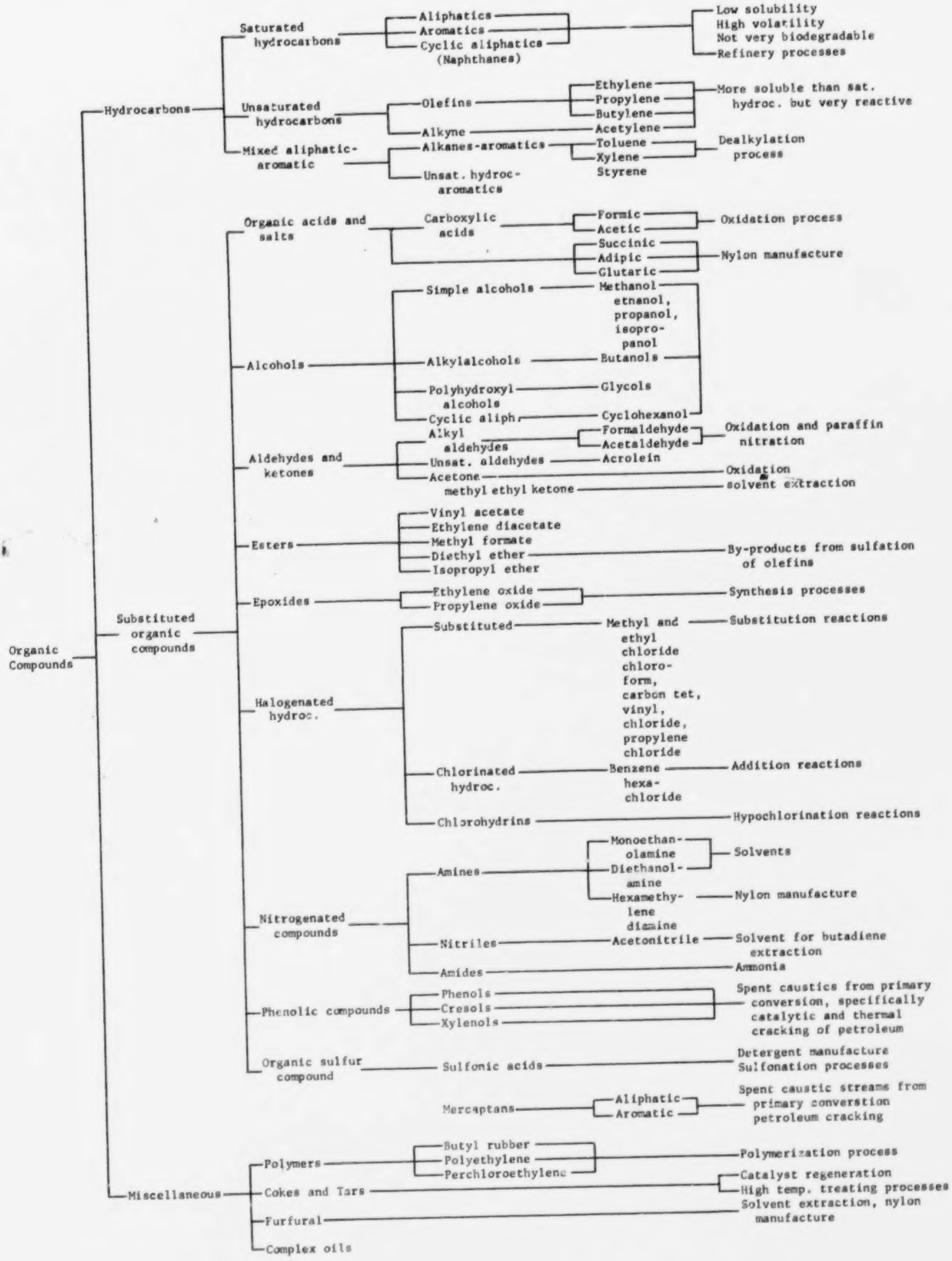

FIGURE 12

CLASSIFICATION OF ORGANIC COMPOUNDS WHICH MAY OCCUR IN PETROCHEMICAL WASTESTREAMS

POLLUTIONAL EFFECTS OF PETROCHEMICAL WASTES

This section evaluates the effect of petrochemical pollution as it applies to mankind, aquatic biota, downstream users, and water and land use planning. Also included are explanations of the parameters most commonly used to describe petrochemical pollution and analytical techniques employed to evaluate the nature and amount of specific pollutants derived from the petrochemical industry.

CONVENTIONAL POLLUTIONAL PARAMETERS

It is generally considered impossible to express waste characteristics in terms of the quantities of pollutant produced per unit of product produced. This is true because the age of the plant, operational procedures, etc., result in infinite variations. Therefore, the use of general pollutional parameters is employed and provides a common yardstick for the assessment of the pollutional characteristics of an effluent stream. The more important parameters are discussed below.

Acidity in a petrochemical waste can be contributed by both organic and inorganic compound dissociation. Most mineral acids found in petrochemical wastes (sulfuric, nitric, phosphoric) are typically strong acids while the most common weaker acids include organic acids such as carboxylic acid and the inorganic acid, carbonic acid.

Both inorganic and organic compounds can contribute to alkalinity, but the most important alkaline wastes in the petrochemical industry are the spent caustics containing sodium, calcium, and potassium salts.

Color and turbidity are physical properties related to the concentration of certain solutes and suspended particles in wastewaters. Color and turbidity diminish light penetration in natural water, thus, reducing the number of photosynthetic organisms such as algae. Although this is sometimes desirable, it is nonetheless considered as a pollutional effect in this context.

The hydrogen ion concentration in an aqueous solution is represented by the pH of that solution. Most plants and animals function most effectively at neutral or near-neutral pH levels. Values outside the neutral range of pH five to pH nine will adversely affect most aquatic life; therefore, pH is a valid indicator of the toxic potential of a waste due to excessive acidity or alkalinity. The pH value also can serve as an indicator of the corrosive potential of a process effluent.

Soluble and dissolved organic materials constitute the most significant category of pollutants present in petrochemical wastewaters. In order to predict the polluting potential of organic-laden wastewaters, it is necessary to have some quantitative parameter. Because the oxygen demand presents one of the major concerns in organic waste control, the most commonly used parameters measure the chemical or biological oxygen demand potential of the wastes. Recently, a rapid and simple method of determining total organic carbon has been introduced which measures the polluting potential in terms of organic carbon present rather than molecular oxygen required.

Biochemical oxygen demand (BOD) is a measure of the biologically oxidizable organic material in a wastewater. Ideally, the BOD should represent the oxygen demand which is exerted during the microbial oxidation of organics in the waste, either in a biological treatment process or in a receiving body of water. Because BOD is the oldest and most common organic material, most effluent quality standards are based on allowable BOD effluents concentrations. The BOD value is subject to many variables and records only the biologically degradable fraction of the organics.

The oxygen required to chemically oxidize the organic compounds in a wastewater is termed the chemical oxygen demand (COD). This method oxidizes many organic compounds present in a petrochemical wastewater.

Total organic carbon (TOC) is the measure of all organic carbon present in a wastewater. Although there are still unresolved problems associated with this test, it may well become one of the more important methods of determining the organic content of wastewaters because it measures completely all organic constituents. TOC, in combination with COD and BOD, is probably ideal for determining the wastewater's true organic nature.

The immediate oxygen demand (IOD) is exerted by compounds which react immediately with the dissolved oxygen when they are introduced into solutions containing oxygen. Such compounds include sulfides, thiosulfates, sulfites, nitrites, ferrous iron, and aldehydes.

Solids material in waste streams can be either organic or inorganic and may be dissolved or suspended. Dissolved organic solids are capable of causing color, taste, odor, and oxygen demand at low as well as at high concentrations. Certain forms of inorganic dissolved solids also represent various forms of potential pollutants.

Surface active agents are compounds which tend to concentrate at an interface, arranging their molecules in such a manner as to form a film along the interface. This surface-active property enables them to reduce the surface tension of liquids, emulsifying dirt and oily materials. The major concern with this parameter has been the degree of foaming caused in treatment units and the receiving waters.

Temperature - Thermal pollution has created serious problems in the last few years. The primary effects are biologically related although certain downstream users could also be affected economically because of elevated water temperatures.

Many compounds present in petrochemical wastes are toxic not only to aquatic life but higher animals and plants as well. The bioassay test is commonly used to assess wastewater *toxicity*. Various BOD and Warburg tests can be used to establish the toxic effects against various microorganisms.

Miscellaneous Pollutant Parameters - Other parameters necessary for evaluating optimal treatment methods include analyses of oils, phenols, inorganic ions, nitrogen in its various forms, volatility, and heavy metals.

EFFECTS OF POLLUTION ON RECEIVING WATER

Many pollutional effects of wastes are interrelated. Gross biological and physical changes in a body of water receiving wastes are usually associated with physiological effects on the aquatic organisms in the water.

Aesthetic Effects - The most aesthetically unappealing situation in water receiving waste discharges is usually attributed to unsightly and odoriferous conditions, the most obvious being the anaerobic decomposition of organic materials (66). Other odors may eminate directly from contaminants such as hydrogen sulfide and mercaptan in the waste stream. Visible effects constitute another aesthetic effect of pollution. Rubber particles from synthetic rubber manufacture are insoluble, relatively non-biodegradable, and floatable. Small amounts of oil give an iridescent sheen to a body of water. Surface active materials in petrochemical wastes, principally from detergent manufacture, can cause foaming in a receiving water. Many organic and inorganic compounds found in petrochemical effluents can impart undesirable color to these waters.

Biological Effects - The most prominent effect of biodegradable organic matter is the biochemical oxygen demand which it exerts on the receiving water. When large quantities of organic matter are involved, the rate of oxygen demand by aerobic processes may exceed the rate of oxygen replenishment from atmospheric or photosynthetic sources. This oxygen deficit may cause anaerobic conditions to prevail, exerting a deleterious effect on aerobic species present, including microorganisms as well as fish and other higher animals. Thermal pollution may result in higher temperatures which increase the rate of biological activity and decrease the net transfer of oxygen to the water from the atmosphere. High temperatures are also lethal to many species of microorganisms and fish.

The net biological effect of petrochemical waste pollution is a change in the environmental conditions of the receiving waters. Changes in the microbial population (bacteria, algae, protozoa), which are important members of the food chain may indirectly affect larger species. Polluted water often favors the growth of one species of organism over others. Pollution may not acutely affect the organisms present but may alter their reproductive patterns affecting the progeny and living habits of aquatic organisms and result in erratic patterns of behavior.

Other effects which are closely related to the aforementioned include recreational facilities and land development, which may be impaired due to the aesthetic aspects. Navigation also can be hindered because of sludge banks deposited in the waters and because of corrosive conditions caused by acidic discharges into the receiving water.

EFFECTS OF POLLUTION ON WATER USE AND REUSE

Various petrochemical pollutants, both chemical and physical, may affect the potential future uses of wastewaters or receiving water.

In-plant reuse of process water and recirculation of cooling water is now common practice in many petrochemical plants. Such reuse often requires demineralized water to the level that even trace quantities of organics or inorganics may be considered as pollutional. The most important consideration for cooling water use is preventing the deposition of precipitates in water pipes and in the process coolers (20). The principal precipitates include calcium carbonate, magnesium carbonate, and calcium sulfate. Cooling water generally should not create excessive biological growth and should be noncorrosive.

Domestic, Agriculture, and Industrial - The United States Public Health Service has prepared a list of recommended drinking water standards which prescribe limits for many potential petrochemical pollutants. Bases for the standards include both health and aesthetic considerations (118).

Water used for livestock and crop irrigation must be free of toxic materials. Heavy metals and high concentrations of inorganic dissolved solids may be detrimental to plants and animals, and high salinities may affect different crops adversely. Sodium, an important constituent of spent caustic effluents, reacts with soil to reduce its permeability. Control is therefore necessary. (The water quality requirements for irrigation purposes are shown in Table 5.)

Groundwater - During the three-year period from 1957 through 1959, twenty-two states reported groundwater pollution by oil or petroleum products, and 15 states reported cases of pollution involving various other chemical contaminants (6). Disposal wells, lagoons, and surface dumping were the most important potential sources of petrochemical wastewater pollution cited in the report.

PHYSIOLOGICAL EFFECTS

In a general sense, almost every effect of pollution can be considered as physiological. Even aesthetic effects can be considered physiological in that they act on the senses of man to produce a reaction. The physiological effects as discussed herein include those which are most prevalent to the observer, namely, taste, odor, and toxicity.

TABLE 5

WATER QUALITY FOR SELECTED AGRICULTURAL USES

(Reference 108)

Water Class	Percent Sodium of Cationic Content	EC X 10^6 at $25^{o}C$	Boron, ppm Sensitive Crops	Boron, ppm Semi-tolerant Crops	Boron, ppm Tolerant Crops	Total Solids (mg/l)
Excellent	< 20	< 250	< 0.33	< 0.67	< 1.00	< 390
Good	20-40	250-750	0.33-0.67	0.67-1.33	1.00-2.00	390-1,200
Permissible	40-60	750-2,000	0.67-1.00	1.33-2.00	2.00-3.00	1,200-3,100
Doubtful	60-80	2,000-3,000	1.00-1.25	2.00-2.50	3.00-3.75	3,100-4,700
Unsuitable	> 80	$> 3,000$	> 1.25	> 2.50	> 3.75	$> 4,700$

Taste and Odor - The senses of taste and odor are virtually inseparable in most cases (17). Many compounds in petrochemical wastes cause tastes and odors at very low concentrations with the synergistic effects of complex mixtures magnifying these effects significantly. A study utilizing the chemicals, m-cresol, n-butanol, pyridine, n-butyl-mercaptan, n-amyl acetate, acrylonitrile, 2-4 dichlorophenol, and acetophenone showed marked synergistic effects. Detectable concentrations of selected petrochemical waste constituents are listed in Table 6. Probably the most common and most objectionable odor-causing compound contained in this list is hydrogen sulfide. Compounds containing nitrogen, principally the amines, are also malodorous and are found in various petrochemical wastes, particularly those discharged from synthetic fiber manufacture (105).

Phenol probably has been the organic chemical most often associated with taste and odor problems. These problems occur when water containing phenols is disinfected by chlorination. Dichlorophenols are formed which give water a characteristic medicinal taste at concentrations as low as one part per billion. Recent investigations have shown that taste and odor problems cannot always be correlated with phenol concentrations, indicating that other organic compounds are often responsible for these conditions (120). For example, chlorinated hydrocarbons have been identified as a major source of taste and odors. A study of a refinery wastewater indicated that the non-polar organic compounds, consisting principally of aliphatic and aromatic hydrocarbons, were the primary sources of odor in the wastewater (90). Organic acids which are found in petrochemical wastes also cause tastes and odors. Recently reported profile studies for wastewaters from twelve different refineries indicated two types of odor characteristics that generally appear to survive waste treatment. These are described as a burnt rubber smell attributed to several series of sulfides and disulfides such as diaryldisulfides and alkyl aryl sulfides, and burnt-oily odor identified with methylated polycylic hydrocarbons such as dimethyl naphthalene and dimethyl anthracene (21).

Some organic chemicals can cause the flesh of fish to become "tainted," rendering the fish useless as a food source. A few chemicals which may be found in petrochemical effluents and are able to cause these effects are listed in Table 7.

Toxicity includes the effects of pH, lack of dissolved oxygen, high temperature, and high dissolved solids as well as compounds which are classified as poisons. It is the poison effect which will be considered here. The classifications of toxic action are established on the basis of the rate of action of the toxicant, the duration of the symptoms, and the rate of intake of the compound (49). Acute toxicity is characterized by the rapid onset of negative physiological effects after exposure to the toxic concentration of a compound. Chronic toxicity is usually manifested by the appearance of negative physiological effects after a prolonged dosage of a chemical at concentrations below the acute level.

While the toxic effect of petrochemicals on man is of great interest, concentrations of these chemicals in water is usually so low that their principal toxic effects on man are generally chronic. Carcinogenesis is

TABLE 6

DETECTABLE CONCENTRATIONS OF SOME PETROCHEMICAL COMPOUNDS CAUSING TASTE AND ODOR IN WATER

Compound	Detectable Concentration (mg/l)	Reference
Ammonia	0.037	63
Amyl Acetate (iso)	0.0006	63
Benzaldehyde	0.003	63
Carbon Disulfide	0.0026	63
Chlorophenolics	0.001 - 0.1	18
- Monochlorophenol	0.00018	63
Dimethylamine	0.6	105
Ethyl Mercaptan	0.00019	18
Formaldehyde	50.0	18
Furfural	4.0	18
Hydrogen Cyanide	0.001	63
Hydrogen Sulfide	0.001	63
Methyl Mercaptan	0.0011	63
Nitrobenzene	0.03	63
Petrochemical Wastes	0.015 - 0.1	63
Phenolics	0.25 - 4.0	18
Phenyl Ether	0.013	18
Picolines	0.5 - 1.0	18
Refinery Hydrocarbons	0.025 - 0.05	18
Sulfur Dioxide	0.009	63
Xylenes	0.3 - 1.0	18

TABLE 7

SOME ORGANIC CHEMICALS CAUSING ADVERSE TASTES IN FISH

Compound	Type Fish Tested	Approx. Concen. Causing Taste (mg/l)	Ref
Phenol	Trout, Carp	25*; 1.0	63, 107
Cresols	Trout, Carp	10	63
1, 3, 4-Xylenol	Carp	5	63
1, 3, 5-Xylenol	Rudd	1	63
1, 2, 4-Xylenol	Rudd	1	63
Pyrocatechol	Carp	2.5	63
Resorcinol	Carp	30.0	63
p-Toluidine	Rudd	20.0	63
Pyridine	Carp, Rudd	5.0	63
Quinoline	Carp	0.5-1.0	63
Naphthalene	Rudd	1.0	63
α-Naphthylamine	Rudd	3.0	63
o-sec butyl Phenol	Not Reported	0.3	107
p-tert butyl Phenol	Not Reported	0.03	107
o-Phenylphenol	Not Reported	1.0	107
o-Chlorophenol	Not Reported	0.015	107
p-Chlorophenol	Not Reported	0.05	107
2,4-Dichlorophenol	Not Reported	0.005	107
Diphenyloxide	Not Reported	0.05	107
Acetophenone	Not Reported	0.5	107
Styrene	Not Reported	0.25	107
α-Methylstyrene	Not Reported	0.25	107
Isopropylbenzene	Not Reported	0.25	107
Ethyl Benzene	Not Reported	0.25	107
β β'-Dichloroethylether	Not Reported	1.0	107
o-Dichlorobenzene	Not Reported	< 0.25	107
Toluene	Not Reported	< 0.25	107
Cresylic Acid (m,p)	Not Reported	0.2	107
Kerosene	Not Reported	0.1	107

* Above Toxic Limit

** Test Fish Not Reported

the chronic toxic effect which has probably received the most attention. Certain polynuclear aromatic compounds, such as aromatic amines, and aromatic nitro-compounds have been shown to cause cancer. The complex hydrocarbons and tars have also been indicated as possible carcinogenic agents (57). The use of carbon chloroform extract from water samples has been proposed as a basis for limiting the exposure of man to these compounds (40). Some research has considered the toxicity effects of surface-active materials in water and indicated that these compounds do not have chronic effects on higher animals at concentrations up to 1,000 mg/l in drinking water (82).

The toxic effects of chemical compounds to aquatic microorganisms are extremely important and a great deal of data is available concerning these effects. The extinction of any of these organisms attributable to toxic chemicals will have a profound adverse effect on the general ecology of the aquatic system. Detailed investigations of the toxicity of certain organic chemicals to algae have recently been reported (56; 107). Data from studies considering structurally similar fatty acids, alcohols, and aldehydes indicate that relative toxicity is somewhat dependent upon molecular structure. For example, straight-chain organics seem to be more toxic than those with branched-carbon chains (107). Certain phenolic compounds and pesticides reduce the chlorophyll concentration and photosynthetic activity of Chlorella pyrenoidosa (56). Additionally, nitrated and halogenated phenols are more toxic than alkylated and aminated phenols, and the insecticide Lindane was found to be about 100 times as toxic to Chlorella pyrenoidosa as was phenol.

Fish are the test animals most frequently used in determining the toxicity of aqueous wastes. This is true for two reasons: (1) they are relatively easy to use and control in the laboratory and (2) their response to toxic materials is one of the more valid indicators of the true toxicity in natural waters. The laboratory bioassay is the most popular method for defining the acute toxicity of specific compounds to fish. The most commonly accepted fish toxicity parameter is the median tolerance limit (TL_M) which is the concentration of the test compound at which 50 percent of the test fish survive for a selected time interval.

The avoidance of polluted water by fish has been suggested as a toxicity parameter (61). However, several problems develop when avoidance was used. In many cases, fish do not reliably avoid waters containing lethal concentrations of particular toxicants (25). Carp, for example, consistently entered an ammonia contaminated portion of a stream although large numbers were killed (19).

IDENTIFICATION AND MONITORING METHODS

Standard analytical tools used for wastewater analysis (COD, BOD, etc.) are inadequate for evaluating the effects of pollutants or for predicting their occurrence. New analytical methods must be developed so that low-level contaminants can be traced from the petrochemical processes through the waste system and into the aquatic environment. The two general types of analytical categories include chamical techniques and biological methods. Chemical techniques are used principally to measure low-level contaminants causing color, taste, and odor while biological methods are employed to observe toxic or inhibitory effects of waste discharges to the aquatic biota.

Chemical Methods of Analysis - These can be broken down into two categories, inorganic and organic.

Inorganic analyses often require two steps, a separation and/or concentration step followed by the identification and quantification of the desired compound. The separation processes most often used for inorganic compounds are volatilization, precipitation, liquid-liquid extraction, and adsorption (77). Chromatography and ion exchange are the two most commonly used adsorptive methods of separation. Gravimetric procedures are often used if the compound in question can be isolated and maintained in a measurable form. Titrimetric methods are used for several inorganic analyses, the most common of which measure alkalinity, acidity, and calcium and magnesium ions using ethylene diaminetetraacetic acid (EDTA).

Spectroscopic methods are also used to measure many inorganic compounds. Flame photometry can be used to measure the alkali and alkaline earth metals such as sodium and potassium (12). Emission spectroscopes using high temperature arcs and rarefied gases can be used to measure metals in the parts per billion concentration range (77). Absorption spectrometers are available and can be used to identify and measure inorganic compounds from trace concentrations to fairly large quantities. In aqueous samples, interferences are common, and separation procedures must often be employed. Infrared spectroscopy can be used to measure inorganic compounds, but has not been used extensively in water analyses. Gamma-ray and x-ray spectrometry also have been used to a limited extent in water analyses.

Methods involving the measurements of the electrical properties of systems are used for inorganic analyses of aqueous systems. Polarography is not applicable for analyzing inorganics, but can be used for measuring heavy metals more rapidly and avoiding many of the interferences associated with the corresponding colorimetric methods.

Organic Analysis - Prior to analysis, most organic compounds in natural waters must be concentrated and, for some analyses, separated. Several methods are available for concentrating trace organic compounds, including adsorption on carbon filters, liquid-liquid extraction, freeze concentration, distillation, and various combinations of these techniques (18). The two most commonly used organic analytical techniques are spectroscopy and chromatography.

Spectroscopic techniques are probably the most commonly used methods of organic analyses, the principal ranges of the spectrum used being the ultraviolet, the visible, and the infrared. Ultraviolet spectroscopy is often used in water and wastewater analysis, but it is often difficult to determine the molecular structure of unknown compounds due to interferences which prevent discrete adsorption bands (18). Differential spectroscopy can be used to eliminate interferences by other compounds in a wastewater sample. Spectroscopy in the visible range, known as colorimetry, is widely used. Infrared spectroscopy is finding increasing application in waste analysis and is often used in combination with other techniques to identify the molecular structure of organic contaminants. Differential absorption methods generally are utilized in infrared spectroscopy, and samples can be analyzed in the solid, liquid, or gaseous form. Mass spectroscopy, in combination with other analytical techniques, also has been used to elucidate the structure of organic contaminants.

Gas-liquid chromatography is another analytical tool used in water analysis. The development of the sensitive flame-ionization, electron-capture, and electron-affinity detectors has made gas-liquid chromatography applicable for identifying most classes of organic compounds (18). Electroncapture detectors have been used to identify the organic phosphate, chlorinated hydrocarbon, and organic sulfur pesticides in the microgram-per-liter concentration range. One of the most promising uses of gas-liquid chromatography and the flame-ionization detector is the continuous monitoring of process and treatment plant effluents. Gas-liquid procedures have been used extensively to separate organic compounds which are subsequently analyzed by other techniques such as mass spectroscopy.

Both thin-layer and paper chromatography have been employed to some extent for the determination of trace organic compounds in water. Some compounds can be separated and identified in microgram-per-liter concentrations by paper chromatography. Paper chromatography is a slow procedure, and it is not extremely accurate for quantitative measurements. Thin-layer chromatography, however, has the separation powers of paper chromatography.

Combinations of the more important analytical techniques used in the identification and measurement of trace organics in water samples are often used. Infrared spectroscopy, nuclear magnetic resonance, and gas chromatography-mass spectroscopy have been used to determine the structures of some compounds derived from petrochemicals (24). Carbon absorption, liquid-liquid extraction, silica gel adsorption chromatography, and gas chromatography were used to identify petroleum products in four pollution incidents (70).

Biological Methods of Analysis - Procedures have been proposed to measure the biological effects of a waste in the aquatic environment *in situ*. Continuously operating biological monitoring systems have two advantages over their chemical systems counterparts: namely, they monitor the entire environment rather than sampled portions, and all the environmental variables are considered rather than recording each characteristic separately (26). Another environmental biological monitoring system assigns a "biotic index" to the natural waters receiving pollutants (19). Based on the macro-invertebrate organisms (insects, tubificial worms) in the receiving waters, the biotic index can be calculated from samples taken by any method which gives an accurate representation of population densities. Bioassay techniques using organisms other than fish also have been proposed because it is now realized that toxic effects of a compound on aquatic plants and invertebrates are equally as important as the effects on fish. The use of bacteria, protozoa, and algae present in the Winogradskey column has also been suggested as a toxicity indicator (58). Protozoa are also effective for toxicity determinations, and several bioassay techniques have been used with protozoa as the indicators of toxicity.

TREATMENT AND CONTROL OF PETROCHEMICAL WASTES

The treatment and control processes discussed herein are categorized as (a) reduction of waste strength by in-process and in-plant control measures, (b) physical treatment processes, (c) chemical treatment processes, (d) biological treatment processes, and (e) ultimate disposal techniques.

INTERNAL IMPROVEMENTS

The ideal method of controlling petrochemical pollutants is to eliminate them at the sources. This reduces the cost of waste treatment and in many cases provides valuable economic gains in the form of reduced losses of expensive petrochemicals and reduced intake of makeup water.

Reduction of Raw Material Losses - The losses of hydrocarbon raw materials from storage, transport, and processing facilities are an important source of water pollution in the petrochemical industry. Several improvements can be made by the industry to reduce the magnitude of these losses. The evaporation of light hydrocarbons from storage tanks can be controlled by floating roof tanks and the use of tank vents with vapor recovery lines. Purge lines used for process start-up and shutdown can be connected to vapor recovery systems (78). The hydrocarbon losses from vacuum jets can be reduced by installing refrigerated condensors ahead of the jets (60) or by connecting the jet exhaust to vapor recovery systems (78). Pipeline systems should be used to transfer raw materials whenever feasible in order to minimize transfer losses. Probably the most important source of hydrocarbon raw material loss is from malfunctioning equipment, leakages, etc. These losses can be corrected only by careful in-plant control.

Recovery of Usable Reaction Products - By-products represent a significant pollutional fraction of petrochemical wastewaters. In many cases, by-product recovery from the process wastes is justified, not only in terms of producing a product, but also in reducing the pollutional load to the waste treatment facility. The recovery of sulfur, for example, from petroleum hydrocarbons minimizes the sulfide and mercaptan pollution. The Claus process (11) and a catalytic combustion process (10) are currently used to convert hydrogen sulfide to elemental sulfur, thus, obtaining a reusable product.

Other sources of usable materials found in petrochemical wastes include catalyst complex metals and the tars from catalytic processes. Usually, the recovery of materials from the tars does not result in a direct profit to the petrochemical plant, but it may prove economically justified by reducing the pollutional discharge. Alkaline wastes from caustic washes are most significant. Some spent caustic solutions containing sulfides, phenolates, cresolates, and carbonates are marketable (76). Spent caustics which contain large amounts of phenols and cresols can be sold to processors who separate and purify the cresylic acid fractions for commercial use (20). Sodium sulfide can be separated from spent caustics high in sulfides and marketed. Spent caustics can also be regenerated for reuse in washing processes by steam hydrolysis, electrolysis, air regeneration, and the use of slaked lime (76).

The recovery and recycling of process effluents containing unreacted raw materials is common to most petrochemical processes in which the process reaction is incomplete. Many of the secondary reaction by-products are also valuable either for use within the petrochemical plant or as marketable products. Some of the possible uses for by-products produced in three common petrochemical processes are shown in Table 8. The recovery and reuse of oils is very common in the petrochemical industry. Recoverable oils are reprocessed while those which are uneconomical to purify are used as fuels. Solvent recovery is practiced also, especially when the high costs of solvents are redeemable.

Process modifications can be classed as (a) process selection, (b) prevention of product and chemical losses, and (c) modified operating conditions (9). If waste control is considered during process design, it often can be an important factor in the economics of operation. The substitution of continuous processes for batch processes tends to eliminate peak discharges of wastes, thus reducing the cost of treatment required for the waste. The use of downgraded chemicals in processes which do not require high-quality reactants facilitate both process and waste control. This type of design often utilizes the waste effluents from one process as reactants in another.

Water reuse is often one of the most effective and economical means of decreasing the waste discharges from a petrochemical plant. In addition to reducing water costs and waste treatment costs, water reuse increases the flexibility for plant expansion. Small quantities of concentrated wastes produced by reuse are easier to handle than larger quantities of dilute wastes, and the plant benefits by more freedom from upstream users (28).

Potential applications of water reuse include the utilization of poorer quality cooling and boiler water and also the reuse of contaminated steams in stripping operations (87). Water use systems are classified as multiple recycle and cascade, but most frequently combinations of these schemes are employed.

TABLE 8

USABLE SIDE PRODUCTS FROM SOME TYPICAL PETROCHEMICAL PROCESSES

(Reference 89)

Primary Product	Side-Products	Use
Butadiene:	Residue Gas (Hydrogen, methane, ethane ,carbon dioxide)	Fuel
	Propane and Propylene	Feedstock for Ethylene, Alkylation
	Butane and Butenes	Recycle for Butadiene Manufacture; Feedstock for Alkylation
	Aromatic Oils	Resin or Plastic Manufacture
Ethylene:	Residue Gas (Hydrogen, Methane)	Fuel
	Acetylene	Fuel for Welding Feedstock for Several Petrochemical Processes
	Ethane	Recycle for Ethylene Manufacture; Cracking Feedstock; Fuel
	Propane and Propylene	Propane Recycle for Ethylene Manufacture; Feedstocks for Several Petrochemical Processes (Alcohol, Alkylation, Polypropylene, etc.)
	Butane and Butylene	Feedstock for Synthetic Rubber Aviation Gas; Recycle to Cracking Process
	Aromatic Concentrate	Resin and Plastic Manufacture
	Heavy Oils and Tars	Refinery Charge Stock Fuel

TABLE 8 (Continued)

USABLE SIDE-PRODUCTS FROM SOME TYPICAL PETROCHEMICAL PROCESSES

Primary Product	Side-Products	Use
Ammonia:	Carbon Dioxide	Dry Ice, Bottled CO_2 Fuel Methanol Manufacture
	Helium	Lifting Gas Inert Gas
	Argon	Inert Gas

Steam used for the stripping and quenching of process streams is an important source of waste. Condensates with high sulfide contents can be partially oxidized to sulfate and then used to generate low-quality stripping steam, although oxygen-demanding thiosulfates may be present. Another condensate reuse scheme has been described in which phenolic condensate from an olefin unit is washed with the fresh hydrocarbon feedstream, thus removing the phenol from the condensate (78). Other volatile hydrocarbons are then steam-stripped from the condensate and reused to generate additional steam. A potential source of water for reuse in the petrochemical plant is for main boiler use. Boilers can often tolerate high dissolved solids concentrations, depending on the type of dissolved solids and the boiler design. Oils do not seem to deposit in boilers if chelating agents prevent other depositions from forming; thus, the oils are steam distilled or leave the boiler with the blowdown.

In-Plant Control - Operational control is one of the most important facets of pollution abatement. In-plant operational control includes (a) maintenance of pipes, valves, fittings, pump seals, etc., to prevent leaks; (b) education of all plant personnel as to the effects of accidental and careless losses of materials; (c) changes in selected operational procedures; and (d) a highly developed monitoring system to detect the sources and occurrences of pollutants within the plant. A continuous monitoring program for important plant sewers can prove invaluable in locating malfunctioning process units and leaks.

Waste Stream Segregation - Three main segregated collection systems are normally used in petrochemical plants (9):

a) area drains which carry off unpolluted cooling water and storm runoff from uncontaminated areas;

b) a contaminated water system which contains process waters, polluted cooling waters, and storm water runoff from contaminated areas; and

c) a sanitary sewerage system to collect plant domestic wastes.

Segregation of many process streams may be necessary due to the incompatability of certain waste components. Wastes with high solids concentrations are usually segregated from oily streams since suspended solids tend to decrease the efficiency of oil separation units. Suspended solids also can interfere with oil recovery by increasing the solids contents of separator skimmings (9).

PHYSICAL TREATMENT PROCESSES

The types of physical treatment processes most commonly used in the treatment of petrochemical wastes include gravity separation, flotation, stripping processes, adsorption, extraction, and combustion. The waste from a petrochemical plant may require a combination of these processes if proper treatment is to be provided.

Gravity separation includes the removal of materials less dense than water such as oils and air-entrained particulates by flotation and the removal of suspended materials which are more dense than water by sedimentation. Sedimentation and flotation techniques commonly employ chemical conditioners to enhance the separation process. Many wastewaters from petrochemical operations contain significant quantities of free and emulsified oil which must be removed prior to subsequent treatment. Free oils are much easier to remove if their concentration is high. Slop oils which are recovered by the separation process can be cleaned and reused in various processing operations. Probably the most commonly employed separator design is that presented by the American Petroleum Institute (8). Reported efficiencies of some oil separators operated by the petroleum industry are given in Table 9. Although some reduction in chemical oxygen demand (COD) can be expected due to removal of oils and tars, little or no biochemical oxygen demand (BOD) removal will be prevalent.

Oil emulsions present the biggest problem of oil-water separation because they are not easily separated in gravity separators and other conventional separation devices. Emulsifying agents prevent the oils from coalescing and separating from the water phase. These emulsifying agents are surface-active agents and include catalysts, the sulfonic acids, naphthenic acids, and fatty acids, as well as their sodium and potassium salts. In an alkaline medium, calcium and magnesium salts form finely divided suspended solids which stabilize the emulsions (83). Sources of oil emulsions within a petrochemical plant include (a) crude oil desalting water, (b) condensates from distilling operations, (c) wash waters which follow caustic or acid chemical treating operations, (d) cooling waters from direct-contact condensors, (e) detergent manufacturing processes, and (f) equipment cleaning operations (8).

In order to separate the emulsified oils from the wastewater, the emulsion must be broken. The application of heat and pressure is probably one of the more effective methods used in de-emulsification of a waste (8). Distillation methods, in lieu of the heat requirements, are also effective in breaking emulsions as are filtration, acidification, and electrical methods.

Sedimentation processes are utilized in the pre- or primary treatment of petrochemical wastes with high suspended solids concentrations, in secondary clarification, and for sludge thickening. Petrochemical wastewaters high in colloidal material must be chemically treated before adequate separation by sedimentation can be obtained. The removal of solids and oils from petrochemical wastewaters and the concentration of sludges can often be accomplished using the air flotation process. Air is dissolved under pressures of 30 to 60 psig with the wastewater to be treated. When the waste is then exposed to the atmosphere, minute air bubbles are released from solution and carry the suspended materials to the top of the tank. Gravity oil separators usually precede flotation units in most industrial applications. One of the big advantages of flotation over sedimentation is the shorter detention time required to clarify a waste by flotation, resulting in a unit of considerably smaller size.

TABLE 9

TYPICAL EFFICIENCIES OF OIL SEPARATION UNITS

Oil Content		Oil Removed (%)	Type	COD Removed (%)	BOD Removed (%)	Phenol Removed (%)	Ref
Influent (mg/1)	Effluent (mg/1)						
7,000-8,000	125	98-99+	Circular	-	-	-	115
3,200	10-50	98-99+	Impounding	0	-	-	83
400-200	10-40	90-95	Parallel Plate	-	-	-	59
220	49	78	API*	45	-	55	20
108	20	81.5	Circular	-	-	-	111
108	50	54	Circular	16	0	0	20
90-98	40-44	55	API	-	-	-	20
50-100	20-40	60	API	-	-	-	20
42	20	52	API	-	-	-	20

* API - American Petroleum Institute Standard Design

Stripping processes are used to remove volatile materials from liquid streams. These methods are employed generally to remove relatively small quantities of volatile pollutants from large volumes of wastewater. Stripping is essentially a low-temperature distillation process whereby reduction of effective vapor pressure by the introduction of the stripping medium replaces the high temperature requirement. The two types of stripping agents commonly used are steam and inert gas.

The stripping of hydrogen sulfide and ammonia from sour water is probably the most common use of stripping employed by the petrochemical industry for waste treatment. The major stripping agents used to remove these contaminants are steam, natural gas, and flue gas. Phenols also can be removed from aqueous waste streams by steam stripping which is applicable when a wastewater is subject to short variations in temperature, specific gravity, phenol concentrations, and suspended solids (53).

Volatile organic compounds can be stripped from aqueous wastes by using air as the stripping agent. The stripping rate of a volatile organic compound is a function of temperature, the stripping gas flow rate, and tank geometry (37; 46). Laboratory testing has indicated that most of the BOD removal during the stripping of biodegradable volatile organic compounds was the result of biological action rather than physical stripping (39). If an organic compound is non-biodegradable and volatile, air stripping may be a feasible unit process.

Solvent extraction methods utilize the preferential solubility of materials in a selected solvent as a separation technique. The criteria for effective use of a solvent in wastewater treatment include (a) low water solubility, (b) density differential greater than 0.02 between solvent and wastewater, (c) high distribution coefficient for waste component being extracted, (d) low volatility and resistance to degradation by heat if distillation is used for regeneration or low solubility in liquid regenerants, and (e) economical to use (49). Equipment used for extraction of wastewater include counter current towers, mixer-settler units, centrifugal extractors, and miscellaneous equipment of special design.

Solvent extraction has been found to effectively remove phenols. Tricresyl phosphates are excellent solvents for phenol due to their low solubility in water and their high distribution coefficients for phenol. However, they are expensive and deteriorate at high temperature. The electrostatic extractor employed in one phenol recovery process also recovers usable oil from wastewater which helps to make the process economical (68).

Other solvent extraction processes which have been used by the petrochemical industry include the extraction of thiazole-based chemicals from a rubber processing effluent with benzene and the extraction of salicylic and other hydroxy-aromatic acids from a wastewater using methyl-isobutyl-ketone as the solvent (110).

Adsorption is the process whereby substances are attached to the surface of a solid by electrical, physical, or chemical phenomenon. A carbon media has been the most successful adsorbent in removing certain refractory chemicals from wastewaters. Phenols, nitriles, and substituted organics are also adsorbed by carbon when present in low concentrations. Additionally, benzene hexachloride and other chlorinated aromatics have been removed from pesticide manufacturing effluents by carbon adsorption (47). These chlorinated hydrocarbons can be recovered by regeneration with steam or with benzene.

Combustion processes are often feasible for disposal of petrochemical wastes which may be too concentrated, too toxic, or otherwise unsuitable for other methods of disposal. Combustion may be either direct or catalytic, depending on the waste to be oxidized. Incineration and submerged combustion are both direct combustion methods used by the petrochemical industry.

Submerged combustion has been used successfully in the total or partial evaporation of waste streams as well as concentrating dissolved solids. This method produces an effluent which either has reuse value or which is easier to dispose of than large volumes of the liquid waste. Incineration is the most commonly used combustion process for petrochemical wastes. Recently, fluidized bed incinerators have been used for burning oily sludges (50). The fluidized bed incinerator is reported to provide better controlled combustion with lower requirements for excess oxygen than conventional incinerators for oily sludges. However, incineration occasionally converts a water pollution problem into an air pollution problem. For example, the air pollutants, sulfur dioxide, and hydrogen sulfide (from incomplete combustion) may be released to the atmosphere when petrochemical wastes are incinerated.

Filtration processes are used to remove and concentrate solids on oily materials from a waste stream. A filter can be specifically designed to remove small quantities of these materials as a final step in waste treatment, or it may be used to concentrate a waste so that further treatability of wastewater will be enhanced. Sludges produced by chemical coagulation and clarification of petrochemical wastes are often concentrated using centrifugation or vacuum filtration for easier handling and disposal. If effluent standards imposed on a plant are particularly stringent, a polishing filter employing sand filtration can be used to remove additional suspended material (110).

Miscellaneous Treatment Methods - Evaporation has been used as a method for treating some petrochemical wastewaters. Solar evaporation is feasible in areas with low annual rainfall and a relatively warm climate. Spraying the wastewater into the air also will increase the evaporation rate.

The separation of surface-active agents from wastewater by induced foaming has been investigated in laboratory and pilot plant studies (22). Most of these studies have considered the removal of synthetic detergents from domestic wastes (74). It has been demonstrated that the surface-active agent, naphthylamine, which has little or no foaming ability, could be removed from solution by adding a foaming agent and inducing frothing (62).

CHEMICAL TREATMENT

The use of chemical systems for treating specific petrochemical wastes has been successfully employed. The most common methods for chemically treating petrochemical wastes include neutralization, precipitation, coagulation, and oxidation.

Neutralization and pH Adjustment - Neutralization of petrochemical wastes may be desired for several reasons, including:

a) preparation of a waste for biological treatment,

b) preparation of a waste for direct discharge,

c) pretreatment for efficient coagulation,

d) prevention of attack and corrosion of conveyance or process equipment, and

e) prevention of unwanted precipitation of waste components.

Neutralization implies the adjustment of a wastewater pH to values at or near neutral pH; i.e., pH seven. Types of wastes generally neutralized are (a) dilute acid or alkaline wash waters; (b) spent caustics; (c) acid sludges from alkylation, sulfonation, sulfation, and acid treating processes; and (d) spent acid catalysts (9).

Sulfuric acid is the most common neutralizing agent used to neutralize spent caustic wastes (76). Acid sludges are normally hydrolyzed to free acids prior to their use as neutralizing agents. Spent caustic neutralization with an acid can be designed as a batch or a continuous system. The carbon dioxide in flue gases can also be used to neutralize spent caustic solutions. Flue gas neutralization is economically feasible provided that the gases are available at high enough pressures so that no compressor is required to inject them into the spent caustic solution. Spent acid catalyst and sludges have been spread in pits filled with lime, limestone, or oyster shells for neutralization. It should be noted that pH adjustment is commonly used to facilitate coagulation and precipitation.

Coagulation - Precipitation - The addition of coagulants under proper conditions causes the formation of a settleable precipitate containing waste materials which can be removed by conventional sedimentation or flotation processes. It should be noted that coagulation is always followed by some type of solids-separation process. The most commonly used coagulants are hydrated aluminum sulfate (alum), ferrous sulfate, and ferric salts. The conventional coagulation system utilizes a rapid mix tank followed by slow agitation of the mixture to promote growth of floc particles which settle. The sludge-blanket clarifier, which provides mixing, flocculation, and settling in the same unit, has had many industrial applications because of its compact dimensions.

Coagulant aids are sometimes necessary to promote bridging between floc particles and render the floc more settleable. The most common coagulant aids are activated silica, bentonite clays, the organic polyelectrolytes, and water treatment clarifier sludge. The three types of polyelectrolytes are categorized by their electrochemical nature, specifically, cationic, anionic, and nonionic.

A common application of coagulation in the petrochemical industry is the removal of emulsified oils from waste streams. Suspended solids and turbidity removals are often as high as 90 percent. However, most petrochemical wastes contain dissolved organic compounds which are not easily removed using coagulation methods. Coagulation has been used also to remove metals such as lead and zinc, water-soluble alkyl-aryl sulfonates by lime coagulation enhanced with ferrous sulfate, and low concentrations of sulfide which are precipitated with zinc chloride, ferric chloride, or copper sulfate.

Provisions must be made for the disposal of the sludges formed by the settled precipitates from coagulation-precipitation processes. Landfills are the most common form of inorganic sludge disposal, while organic sludges are usually dewatered by some filtration method and subsequently incinerated or buried.

Oxidation processes are used to treat both organic and inorganic contaminants using oxygen or other chemicals as the oxidizing agents. The oxidation of sulfides to sulfates using steam and air is an effective treatment method; however, wastes containing high concentrations of phenol cannot be treated in this manner because phenols interfere with sulfide oxidation. If large quantities of mercaptans or mercaptides are present in the waste, a reoxidizer may be required to insure complete oxidation (20).

Catalytic oxidation is usually applied when the fuel value of a waste is too low for conventional incineration. The process was originally designed to operate in the vapor phase but has been successfully applied to aqueous wastes. Laboratory studies have shown that dilute aqueous organic wastes could be effectively oxidized at temperatures below 600°C by using a copper-chromate catalyst (51). Investigations have demonstrated that hydrocarbons also could be oxidized by using metal oxide catalysts (102). The initial cost of catalytic oxidation units may be 20 to 30 percent greater than that for conventional incinerators, but for dilute organic wastes the operating costs may be 15 to 20 percent less (9).

Wastes containing sodium sulfite, which has a very high immediate oxygen demand, can be oxidized by bubbling air through the system. Iron catalysts have been employed occasionally to speed the oxidation reaction (110).

The oxidation of sulfite to sulfate will increase the acidity of the waste and require subsequent neutralization. Diffused air has also been used to oxidize metal salts to insoluble hydroxides which were removed by sedimentation (31).

Chlorine has been used successfully to oxidize phenol and cyanide in petrochemical wastes. The oxidation of phenols must be carried to completion to prevent the release of chlorophenols which cause objectionable tastes and odors in drinking water. Cyanides can be oxidized to carbon dioxide and nitrogen by chlorination if the pH is maintained in excess of 8.5 and sufficient chlorine used, thus preventing the release of toxic cyanogen chloride. Chlorine dioxide has been shown to overcome these and other disadvantages of chlorine and hypochlorite oxidation, although this treatment is very expensive.

Ozone has been proposed as an oxidizing agent for phenols, cyanides, and other unsaturated organics because it is a considerably stronger oxidizing agent than chlorine. The chief disadvantage is the high initial cost of ozone generation equipment. Ozone has several advantages, one of which is its ability to react rapidly with phenols and cyanide.

Oxidation of phenols using hydrogen peroxide and ferrous salts has been investigated in the laboratory (38). Treatment of the industrial wastes in this case produced colored effluents which required additional treatment with alum.

Miscellaneous Methods - Ion exchange has been used to remove specific petrochemical pollutants. Quaternary ammonium anion resins have successfully removed phenols in the laboratory (3). However, regeneration of the resin was difficult and uneconomical. Salicylic acid recoveries of 80 percent were obtained from aspirin manufacturing effluents using a caustic-soda regenerated resin (110). Chemical reduction has been used in isolated cases to treat constituents of a waste stream.

BIOLOGICAL TREATMENT PROCESSES

Biological treatment of liquid petrochemical wastewaters is usually the most economical method of reducing its toxicity, organic content, and objectionable appearance. Extensive pretreatment is often required before a petrochemical waste stream can be treated biologically.

The applicability of biologically treating a particular waste is a function of the biological degradability of the dissolved organics present in the wastewater. When considering the economics of a biological treatment system, the time required to biologically degrade the dissolved organics is of primary importance. This degradation rate of an organic compound is a function of the molecular structure of the compound, the genera and species of microorganisms utilizing it as a food source, and the time required for the microorganism to develop the enzymes necessary for substrate utilization.

The biodegradability of an organic compound can be classified in several ways (79). The BOD parameter establishes a relative degree of biodegradability provided that acclimated seed is used for the test. There is much contradictory data relating the molecular structure of a compound to its biodegradability. However, the amenability or resistance of certain classifications of organic compounds to biological oxidation is well documented as described below.

a) Aliphatic or cyclic aliphatics are usually more susceptible to biological degradation than aromatics.

b) Unsaturated aliphatics, such as acrylics, vinyl, and carbonyl compounds are generally biodegradable.

c) Molecular size is significant concerning the biodegradability of an organic. Polymeric and complex molecular substances have shown resistance to biological degradation, part of which is attributed to the inability of the necessary enzymes to approach and attack susceptible bonds within the compound structure.

d) Structural isomerisms in organic compounds affect the relative biodegradability of many compound classes. For example, primary and secondary alcohols are extremely degradable while tertiary alcohols are resistant.

e) The addition or removal of a functional group affects the biological oxidation. A hydroxyl or amino substitution to a benzene ring renders the compound more degradable than the parent benzene, while a halogen substitution causes it to be less biodegradable.

f) Many organic compounds are extremely biodegradable at low concentrations but are bio-static or bio-toxic at higher concentrations.

The relative biodegradability of certain organic compounds is presented in Table 10.

Nutrients - Effective biological treatment of any organic contaminant requires the availability of essential nutrients for the organism. The mineral nutrients required by bacteria are available in sufficient amounts in most wastewaters, but nitrogen and phosphorus requirements are more critical and many petrochemical wastes are deficient in one or both of these elements. Nitrogen (N) and phosphorus (P) requirements for biological treatment have been related to the magnitude of the degradable organic content of wastewater as represented by BOD. Generally, a BOD:N:P ratio of 100:5:1 will provide sufficient amounts of these nutrients. Nitrogen is most readily available in its reduced form as ammonia, ammonium ion, or amino nitrogen. Organic nitrogen, nitrates,

TABLE 10

RELATIVE BIODEGRADABILITY OF CERTAIN ORGANIC COMPOUNDS

(References 72, 73, 81)

Biodegradable Organic Compounds	Compounds Generally Resistant to Biological Degradation
Acrylic Acid	Ethers
Aliphatic Acids	Ethylene Chlorohydrin
Aliphatic Alcohols (normal, iso, secondary)	Isoprene
Aliphatic Aldehydes	Methyl Vinyl Ketone
Aliphatic Esters	Morpholine
Alkyl Benzene Sulfonates w/exception of propylene-based Benzaldehyde	Oil
Aromatic Amines	Polymeric Compounds
Dichlorophenols	Polypropylene Benzene Sulfonates
Ethanolamines	Selected Hydrocarbons Aliphatics Aromatics Alkyl-Aryl Groups
Glycols	Tertiary Aliphatic Alcohols
Ketones	Tertiary Benzene Sulfonates
Methacrylic Acid	Trichlorophenols
Methyl Methacrylate	
Monochlorophenols	
Nitriles	
Phenols	
Primary Aliphatic Amines	
Styrene	
Vinyl Acetate	

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[*] Some compounds can be degraded biologically only after extended periods of seed acclimation.

nitrites, and organic compounds containing these forms can also be used, but a considerable expenditure of energy is required to reduce these forms to ammonia nitrogen. Phosphorus is most readily available to the microorganisms as a phosphate.

Neutralization - Most biological treatment systems operate efficiently at pH values between five and nine, while optimum conditions usually fall within the pH six to eight range. Therefore, neutralization or pH adjustment is commonly required in many petrochemical wastewater treatment systems.

Equalization - Petrochemical wastes are particularly subject to wide variations in flow and composition; thus, some form of equalization may be necessary to dampen these fluctuations and minimize transient effects which may adversely affect the biological process.

Pre- and primary treatment may be required to remove certain materials which would adversely affect the biological system. Oils are difficult for the organisms to metabolize due to their low solubility. Inorganic and non-biodegradable organic suspended solids will tend to build up in a treatment system, decreasing the proportion of active biological solids, and thus adversely affecting the treatment efficiency. Sulfides react with dissolved oxygen and reduce the available oxygen to the organisms. Heavy metals are toxic at defined concentrations and must be removed or reduced to safe levels. Also, waste streams with potentially toxic organic compounds should be separated and treated prior to discharge into the biological treatment system.

Temperature - The optimum temperature for most aerobic biological treatment systems is approximately 20 to 35°C (35). High temperatures of waste cause a decrease in oxygen solubility as well as increased oxygen utilization rates.

The activated sludge process is a continuous system where biological growths are mixed with wastewater, aerated, and then undergo biological sludge separation. A portion of the concentrated sludge is then recycled and mixed with additional waste. Completely mixed aeration designs are generally favored over plug flow systems for industrial waste treatment. These effluents discharged from completely mixed activated sludge systems generally are of better quality than those obtained from other biological processes in terms of organic and solids concentrations, but construction and operational costs are usually higher.

Parameters to be considered in the design of an activated sludge system include the fundamental factors of temperature, pH, and nutrient availability as well as the following:

a) the organic loading in terms of BOD applied per day per unit weight of biological solids,

b) the BOD removal kinetics of the specific petrochemical wastewater,

c) the quantity of biological sludge produced including accumulation of primary sludge,

d) the oxygen requirements of the system, and

e) the settleability of the biological sludge and the ease of gravity solids-liquid separation.

A summary of activated sludge plants treating petrochemical wastes, including information concerning the petrochemical products, applied loadings, nutrient requirements, and effluent quality are tabulated in Table 11. It should be recognized that many organic compounds can be chemically oxidized while remaining resistant to biological degradation, therefore being registered as COD but not BOD. The difference between the measured COD and BOD values indicates the magnitude of the organic fraction that is not readily amenable to biological degradation.

Trickling filters are commonly used in industrial waste treatment as "roughing devices" designed to equalize and reduce organic loads to activated sludge or aerated lagoon processes. Trickling filters employ microbial films which are attached to rock or synthetic media to remove organic materials from the wastewater solution. Most filter processes employ recirculation to increase the overall filter efficiency and to minimize shock loadings.

Although BOD removals obtained by trickling filters are usually less than those found in the activated sludge process, toxic effects are not as pronounced or perpetual. Additionally, filter design and operation is relatively simple. The recorded treatment of various chemical and petrochemical wastes using trickling filters is presented in Table 12.

Aerated lagoons are basins six to twelve feet in depth where oxygen is supplied mechanically. The two general types of aerated lagoons are the aerobic lagoon and the facultative lagoon. In the aerobic lagoon, all biological solids are kept in suspension, while sludge settling and consequent anaerobic decomposition are characteristic of the facultative aerated lagoon. In these lagoons, the solids concentration is allowed to reach an equilibrium concentration which depends on the organic concentration of the waste, the synthesis sludge rate coefficients, and the amount of power imparted to the basin liquid. Equilibrium suspended solids normally range from 80 mg/l to 250 mg/l.

High levels of treatment are generally not achieved in the aerated lagoons because of the BOD and COD associated with the effluent suspended solids and the relatively small number of active biological solids in contact with the wastewater. Aerated lagoons are particularly sensitive to transient organic loadings, toxic substances, and temperature changes. A summary of reported data on treatment of petrochemical wastes by aerated lagoons is given in Table 13.

TABLE 11

ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD In (mg/l)	BOD Out (mg/l)	BOD Rem (%)	COD In (mg/l)	COD Out (mg/l)	COD Rem (%)	Organic Loading $\left(\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}\right)$	Nutrients Reqd.	Remarks	Ref
Refinery, Natural Gas Liquids, Chemical Specialties, Sanitary Sewage	4.87	90	20	78	200	90	55	0.1	None	Effl. phenol 0.05 Effl. oil 0.5 mg/l	111
Phthalic Anhydride, Phenol, Salicylic Acid, Rubber Chem., Aspirin, Phenacetin	2.54	45.7	6.1	86.7				0.031	None	Brush Aeration, treats trickling filter effluent, 55% sludge return	110
Refinery, Detergent Alkylate	2.45	345	50-100	71-85.5	855	150-200	76.6-82.5	0.08	PO_4	Phenols in = 160 mg/l Sulfide in = 150 mg/l Lab scale	44
Butadiene Maleic Acid	2.0	2,000	25	98.8	2,990	480	84	0.24	NH_3		34
Butadiene Alkylate	1.5	1,960	24	98.8	2,980	477	98.3				34
Butadiene, Maleic Anhydride Fumaric Acid, Tetrahydrophthalic, Anhydride, Butylene Isomers, Alkylate	1.5	1,960	24	98.8	2,980	51	84	0.24 (MLVSS)	NH_3	Surface aerators wastes contain: alcohols, maleic acid, fumaric acid, cetic acid, C_1-C_4 aldehydes, furfural, water soluble addition products	84

TABLE 11 (Continued)

ACTIVATED SLUDCE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\left(\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}\right)$	Nutrients Reqd.	Remarks	Ref
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)				
Ethylene Propylene, Benzene	1.44	600	90	85	700	105	85		None	Oily waters: C_4-C_{10} oils 90% phenol removal	92
Naphthalene, Butadiene, Phenol, Acrylonitrile, Soft Detergent Bases, Resins, Other Aromatics	0.43	500	60	85-90	600	90	80-85	1.5	NH_3 PO_4	Sour waters: Oil in = 500 mg/l Phenol in = 65 mg/l pH adjustment, preceeded by trickling filter, phenol removal = 99.9%	92
Phenol, 2, 4-D Aniline, Nitro-Benzene, Rubber Chem., Polyester Resins, Misc. Chem.	0.97	370	76	76.2				0.4	NH_3 PO_4	Accelator Pilot Plant Sewage added in ratio 1:600 once a week	80
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oils	0.63	85	10	99	200	75	62.5			Quench waters, polyethylene and benzene wastes: preceeded by trickling filter, effl. phenol 0.01 ppm	95
Refining Processes	0 51-0.63	125	15-25	80-88			65-80	0.28-0.4	PO_4	Phenol removal 85-94%; Oil removal 75-85%; Effl. phenol 0.5 mg/l; Effl. oil 1-2 mg/l; Temp. - 30°C	59
Nylon	0.4	1,540	250	83.8							34
Petroleum Products	0.27	440	5	98.8	500	60	88			Phenol in = 25 ppm Phenol out - 1 ppm	34

TABLE 11 (Continued)

ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\left(\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}\right)$	Nutrients Reqd.	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Acrylic Fibers	0.252	2,260	118-226	90-95				0.4		Wastes contain acrylonitrile, dimethylamine, dimethylformamide, formic acid temp. 35-37°C return sludge 10-50% mechanical aeration	105
Acetone, Phenol p-Cresol, Ditert.-Butyl-p-Cresol, Dicumyl Peroxide	0.216	3,560-4,400	1,030-750	71-83				0.89-1.1		Waste phenol 600 ppm Waste BOD 7,500-8,000 Waste diluted w/ effl. or water; pilot plant	33
Resins-Formalin, Aminoplasts, Phenol-Formald., Epoxy Resins, Textile Aux.	0.2	890	444-266		50-70			0.8-1.2		Diffused-air; domestic waste added; trickling filter follows 100% recycle sludge	98
Ethylene and Propylene Oxides, Glycols, Morpholines, Ethylene-Diamines, Ethers, Piperazine	0.15	1,950	20	99	7,970-8,540	5,120-5,950	25-40	0.51	None	Lab Scale; extended aeration; high non-biodegradable fraction followed by stab. ponds	43
2, 4-D 2,4,5-T (Acid Wash Wastes)	0.1	1,670	125	92.5	2,500	500	80	0.78 (MLVSS)	NH_3 PO_4	1:1 mixture of acid wash streams diluted 9:1 prior to treatment to reduced chlorides, toxicity Lab Scale	42

TABLE 11 (Continued)

ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD In (mg/l)	BOD Out (mg/l)	BOD Rem (%)	COD In (mg/l)	COD Out (mg/l)	COD Rem (%)	$\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}$	Nutrients Reqd.	Remarks	Ref
Cracking, Isomerization of Butane and Naphthene, Alkylation, Benzene, Toluene, Alcohols, Ketones, Cresylic Acids		1,100	55-110	90-95				0.5		90-95% phenol removed; Lab Scale	29
Ethylene, Acetylene			20					0.23-0.33	PO_4	Effl. phenol 0.1 mg/l Effl. oil 1 ppm	59
Nylon Manuf.-Adipic Acid Aaidonitricz Alk. Organics				95			85	1.0-3.0	PO_4 NH_3	NH_4 OH used as nutrient and neutralizing agent waste diluted 2:1	30 86

TABLE 12

TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\left(\frac{\text{lb BOD}_5\text{/day}}{1{,}000\ \text{ft}^3}\right)$	Deficient Nutrients	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Phenol, Salicylic Acid, Rubber Chem.,	2.59	190	58	69.5				40.5	None	Rock Media, recirc. ratio 2.84:1	110
Aspirin, Phenacetin, Phthalic Anhydride	2.59	58	34	41.5				11.8	None	Rock Media, treats effluent from above filter, effluent to act. sludge	
Plastics, Amines, Enzymes	1.06	1,960	37	98.1	2,660	230	91.5			2 filters, followed	34
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oil	0.63	170	85	50	400	200	50	89	None	Plastic filter media followed by act. sludge phenol removal = 95% influent diluted 2:1 w/cooling water	95
Aliphatic Acids, Esters, Alcohols, Aromatics, Amines, Inorganic Salts	0.57-0.86	1,100-2,300	23-470	57-99				42.1-82 (Both filters combined)	None	pH adjusted prior to treatment; 2 filters in series; Recycle on 1st state is 14-21:1	101
Ethylene, Propylene, Butadiene, Benzene, Naphthalene, Phenol, Acrylonitrile, Soft. Detergent Bases, Resins	0.43	1,300			1,500	450	60-70	140	NH_3 PO_4	Sour Waters, Rock Media	92

TABLE 12 (Continued)

TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD In (mg/1)	BOD Out (mg/1)	BOD Rem (%)	COD In (mg/1)	COD Out (mg/1)	COD Rem (%)	Organic Loading $(\frac{1b\ BOD_5/day}{1,000\ ft^3})$	Deficient Nutrients	Remarks	Ref
Pentaerythritoc Waste contains Formaldehyde, Sodium Formate, Methanol, Pentaerthritol	0.118	5,080-5,800	225-232*	95-96*				1st stage 65	NH_3 PO_4 Yes	2 filters in series followed by act. sludge; recycle 40-1 on prim. filter, 13-1 second	32
Resins-Formaum, Aminoplasts, Phenol-Formal, Epoxy Resins, Textile Aus.	0.17 0.03			82.6 89.3				11.7 14.6	None None	Both filters treat act. sludge effluent, Blast furnace slag media Waste contains phenol, formaldehyde, methanol	98
Acrylic Fibers	0.32		13	30-70		49	30-70	50 84	NH_3 PO_4	Waste contains: acrylonitrile and zinc plastic filter media	91
Synthetic Resins-Phenol, Formaldehyde, Fatty Acids, Phthalic Acid, Maleic Acid, Glycerol, Pentaerythritol, H.C. Solvents				95-98				1st stage 85 (as Phenol) 2nd stage 11.6-18.2 gpd/ft^3		Plastic media, 2-stage treatment; Influent: Phenol = 4,500 mg/1 Formaldehyde = 2,000 mg/1 Fatty acids = 800 mg/1 Phthalic and maleic acids = 1,000 mg/1 Eff. phenol = 1.5 mg/1	27

TABLE 12 (Continued)

TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $(\frac{\text{lb BOD}_5\text{/day}}{1{,}000\ \text{ft}^3})$	Deficient Nutrients	Remarks	Ref
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)				
Waste contains Acrylates, Acetone, Inhibitor oils, Alcohols, Esters, H_2SO_4 Organic Acids								51-79	None None	Original loading was lower value, loading increased w/o any adverse effects 15,000 lb BOD_5 removal per day	23

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* Entire Treatment System

TABLE 13

AERATED LAGOON TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\frac{\text{lb BOD}_5}{\text{Acre} \cdot \text{day}}$	Nutrients Reqd.	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Refinery Butadiene, Butyl Rubber	19.1	225	100	55	610	350	43	4,630	PO_4	Followed by stab. pond temp = 32°C 30% COD is non-biodegradable Lab Scale	45
Refinery, Detergent Alkylate	2.45	345	50-100	71-85	855	150-200	77-83	6,300	PO_4	Influent phenols 160 mg/l Influent sulfides 150 mg/l Lab Scale	44
Cyclohexane, p-Xylene, Benzene, Paraffinic Naphtha, o-Xylene Gasoline Nylon Fibers	0.51	100	25	75				400		Surface aeration, waste is extensively pretreated. Followed by pond	64
Chemicals for Lubricating Oils	0.2	465	180	61	1,050	600	43				34

Waste stabilization ponds, which depend on the natural aquatic processes of bacterial and algal symbiosis, have been used successfully to treat petrochemical wastes. These ponds are often designed to polish the effluent from other biological waste treatment processes, but they have been used in some instances to treat entire plant wastes.

Waste stabilization ponds are categorized as being "aerobic," "facultative," or "anaerobic." The BOD removal found in these oxidation ponds is comparable to other biological unit processes, but the COD reduction capacity is often higher. However, highly colored substances reduce sunlight penetration and cause reduced photosynthesis, often affecting COD removal capacities. There also are toxic effects of many compounds on the pond algae which upset the symbiotic algal-bacterial relationship. Operational data on these ponds in the petrochemical industry are given in Table 14.

Miscellaneous Biological Treatment Processes - Cooling towers have been used as biological treatment devices and provide a method for reuse of water through the means of "free" biological treatment. Pilot plant investigations using a percolating sand filter as a biological treatment process have indicated some promise (33).

Multiple Biological Treatment Schemes - The complexity of most biological treatment systems and the associated effluent quality requirements often circumvent single-stage biological treatment. Various combinations of biological processes, therefore, may be employed to achieve the desired effluent quality.

A general sequence of biological wastewater treatment processes is demonstrated in Figure 13 (88).

OTHER METHODS OF DISPOSAL

Dilution - This form of disposal is becoming less and less popular with regulatory authorities. However, certain petrochemical plants are allowed to discharge their wastes to receiving waters without treatment providing:

a) sufficient receiving water is available as a diluent,

b) there are no toxic or refractory compounds in the waste stream, and

c) the assimilative and recovery capacity of the receiving water is adequate.

Joint industrial-municipal treatment has been successful in certain cases, especially where small petrochemical plants are located near large metropolitan areas. Usually, some form of pretreatment is necessary

TABLE 14

WASTE STABILIZATION POND TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading lb BOD_5 $\left(\frac{}{\text{Acre} \cdot \text{day}}\right)$	Nutrients Reqd.	Remarks	Ref
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)				
Refinery, Butadiene Butyl Rubber	19.1	100	50	50	350	200	43	Primary pond 91; Total ponds 46	None	Ponds in series afte aerated lagoon Lab Scale	45
Resins, Alcohols, Amines, Esters, Styrene, Ethylene	5	500-1,000	400-700	20-60				96	None	Anaerobic	13
	5	400-700	25-50	88-96				164	None	Anaerobic	13
	5	25-50	5-30	40-90				5	None	Aerobic	13
Butane, Propane, Nat. Gas, Ethanol, Ethyl Chloride, Polyethylene, Ammonia, H_2SO_4	3.25	150	7-15	90-95	260			75	None	Facultative pond, 18 days detention Infl. $SO_4 = 650$ mg/l	113
Refinery, Detergent Alkylate	2.45	50-100	20-50	50-80	150-200	120	20-40	95	None	After Aerated Lagoon Or Act. Sludge Lab Scale	44
Plastics	1.69	686	186		1,681	590	65			Facultative Ponds	34
Ethylene and Propylene Oxides, Glycols, Morpholines, Ethylenediamines, Ethers, Piperazine	0.15	20			5,120-5,950	4,610-4,450	10-25	25	None	Lab Scale Facultative Ponds to remove some resid. COD. High non-biodegradable fraction. After activated sludge	43
Mixed Petrochemicals				95-99			75-96	100		Facultative ponds	113

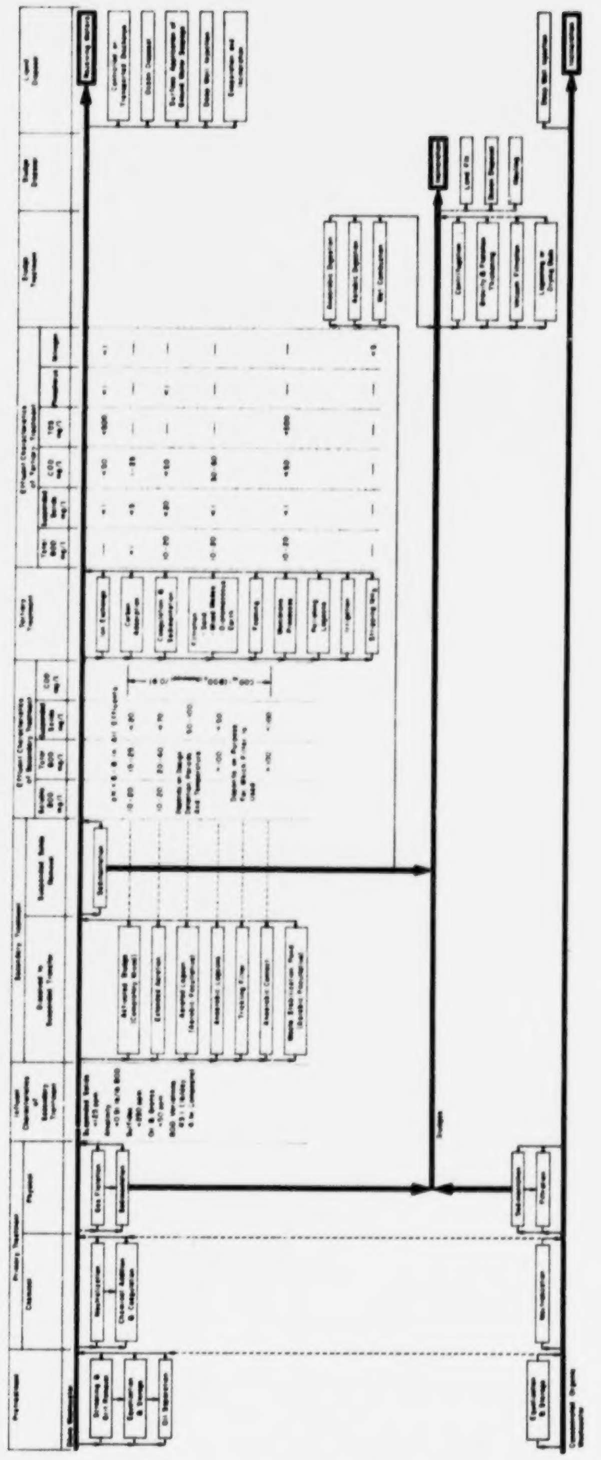

Fig 13 WASTEWATER TREATMENT SEQUENCE / PROCESS SUBSTITUTION DIAGRAM

before the industry discharges into the municipal sewer. It generally has been established, however, that individual treatment offers both economic and political advantages, particularly where large volumes of petrochemical wastewaters are involved.

Disposal wells used for the subsurface injection of wastewater are listed in Table 15. Most of the petrochemical wastes noted in Table 15 must be pretreated prior to injection. The more common formations suitable for injection of wastes include unconsolidated sands, limestones, and dolomites (109). The dangers of contaminating potable water-bearing formations can be assessed by studying the overlying and underlying strata and locating unplugged wells in the contiguous area.

Ocean Outfall - The direct discharge into the ocean is feasible when locations permit. Most liquids flow through outfall pipelines, the distance of discharge from shore depending on the nature of the wastewater, the ocean currents, and shoreline use. Barge disposal is another method of conveying wastes to the ocean for disposal.

Submerged combustion is the burning of a gaseous fuel in a specially designed burner with the burner chamber submerged in the wastewater. This device has been used successfully in totally or partially evaporating waste streams, concentrating any dissolved solids, either which have reuse value or which are easier to dispose of than large volumes of the liquid waste.

A submerged combustion unit reduced 75 percent of the volume of a nylon waste stream, the remainder of which was mixed with other process streams and treated biologically (86). A polymeric waste stream containing suspended synthetic rubber particles, organic solvents, inorganic salts, and synthetic detergents was not amenable to biological treatment and consequently treated by submerged combustion (114). This waste stream was evaporated to about 10 percent of its original waste volume with the resulting slurry emptied to a drying bed. Volatile organic compounds in the polymeric waste, such as alcohols and amines, were oxidized or burned so that no odors were detected in the surrounding area.

Incineration of combustible and partially combustible liquid wastes is often a feasible method of disposing of concentrated process streams. The properly designed incineration system considers time, temperature, and turbulence. Sufficient residence time should be provided to permit complete oxidation of the organic material, the temperature should be high enough for the reaction to proceed, and the system should be sufficiently turbulent to insure that the oxygen in the air is contacted with the dissolved organic material.

Although incineration is a practical means of handling a wide variety of effluents, it should be evaluated only in the light of the total pollution problem, particularly air pollution.

TABLE 15

PETROCHEMICAL WASTE DISPOSAL BY DEEP WELL INJECTION - TYPICAL INSTALLATIONS

Type Waste	Flow (gpm)	Depth (ft)	Injection Pressure (psia)	Formation	Required Pretreatment	Ref
Acrylonitrile and Detergent Manuf. Wastes: COD = 17,500 mg/1; Nitrites = 300 mg/1; pH = 5.4, SO_4 = 10,000 mg/1	650	7,203	Up to 2,000	Sat. Brine, Miocene Sands	Neutralization; Settling and Equalization in Pond; Coagulation pH Adjustment and Clarification; Gravity Sand Filters	92
10-15% NaCl; Diss. Metal Salts; Trace Organics; pH 7.5-8.5	500-600	4 wells:	200	Unconsolidated Brine Sands	Oil Separation; Settling; Pressure Leaf Filtration; Diatomite Filtration	54 31
Refinery and Petrochem. Cooling Water Blow-down Boiler Blow-down, Process Waters	500	1,200	75	Sandstone		48
Petrochem. Waste Organic Nitrogen Nitrites COD = 20,000 ppm pH = 12 Uranium 238	400	6,700	400	Sands	Neutralization, Precipitation - Sedimentation, Filtration	48
Phenolic Waste: COD = 12,000 ppm; 850 ppm Phenol; 150 ppm Oil; pH 10.8	300	6,330	1,000	Sat. Brine, Miocene Sands	Neutralization with H_2SO_4; Clarifier, Pressure Sand Filter	92
Aromatics Phenols 1,000-2,000 ppm COD 10,000 ppm pH 10.7	300	6,100	1,000	Miocene Sands		48

TABLE 15 (Continued)

PETROCHEMICAL WASTE DISPOSAL BY DEEP WELL INJECTION - TYPICAL INSTALLATIONS

Type Waste	Flow (gpm)	Depth (ft)	Injection Pressure (psia)	Formation	Required Pretreatment	Ref
0.3% Acetic Acid and Chlorinated Derivatives	204	3,700	2,000	Miocene Brine Sand	Cool to 150°F. Adjust pH to 4.0-5.0, Settling Coal Filter; Cartridge Filter for Solids $>10\mu$	115 65
Terephthalic Acid Manuf. Cooling and Boiler Blow-down, Process Wastes Containing Organic Acids, H. C., inorganics	150	5,600		Sands	Settling, Filtration	48
Nylon, Ammonia, Olefins, Polyolefins, Refinery, Butadiene, Styrene, Synthetic Rubber 1	Small-96	5,802	800-1,100	Limestone	Conventional Waste Treatment, 0.3% by Volume of Acid, Added Before Injection	71
Cuprous Ammonium Acetate from Butadiene Pond; Caustic Waste from Ethylene Prod., Caustic and Phenols from Refinery	85	>4,000	1,500-2,000		Equalization, Settling	95
Refinery Cooling and Boiler Blowdown, Process Wastes, Brines	50	5,000	600	Sandstone	Settling and Storage	48
Ammonia Prod.	45	1,000	225	Sandstone	API Separator	48

TABLE 15 (Continued)

PETROCHEMICAL WASTE DISPOSAL BY DEEP WELL INJECTION - TYPICAL INSTALLATIONS

Type Waste	Flow (gpm)	Depth (ft)	Injection Pressure (psia)	Formation	Required Pretreatment	Ref
Hydrochloric Acid	40	1,200	14.7	Sandstone	None	48
Detergent Product 32% HCl Benzene Chlorinated HC	35	3,400		Miocene Sands	Dilution with Equal Volume Fresh Water	48
Spent Alkylation Acid-90% H_2SO_4; 7% Oil; 3% H_2O	~ 1	5,100				55
Filtrates and Distillates from Chloromycetin Manuf: BOD_{20} = 45,000 ppm; pH 3.5; Diss. Solids = 50,000 ppm		1,400		Saturated Brine, Sand		2
Saturated NaCl, Conc. Ca-Mg, Liquors, Phenols, Chloro-Phenols, Bis-Phenols, Methocel, Weak Caustic Washes		3,000		Limestone	Suspended Solids Removed	85

ECONOMIC ASPECTS OF PETROCHEMICAL WASTE TREATMENT

The major economic factors considered in waste treatment include:

a) the capital cost of treatment process required to produce a defined quality level of effluent and the operating costs associated with the selected treatment process,

b) the returns to the petrochemical industry resulting from the treatment of its wastewaters in terms of product recovery and water reuse, and

c) the in-plant modifications required to render a treatment process feasible or less costly.

GENERAL CONSIDERATIONS

Attempts to relate capital costs or production units, wastewater flow, BOD, or their parameters have proved quite successful when certain industrial wastewaters are considered. However, the diverse nature of the petrochemical industry and its limited number of wastewater treatment facilities has made it difficult to establish cost function relationships which are applicable throughout the industry. An effective approach for estimating the capital cost of a treatment facility is to calculate the unit costs for each process within the treatment system and to increase the total by a defined percentage to allow for piping, pumping, and related appurtenances, engineering, and contingencies.

The bases for evaluating the capital and operating costs for many of the unit processes used in the treatment of petrochemical wastewaters are tabulated in Table 16. Other variables which affect these cost relationships and are not considered herein include: (a) geographical location, (b) climatic conditions, (c) area labor and materials cost fluctuations, (d) land cost factors, and (e) over-design considerations.

Cognizant of these restraints, a series of capital cost-waste flow relationships have been prepared (20; 36; 37; 88; 99). These graphs have been developed based on 1968 construction costs (ENR 1,030) but are given only in the Detailed Edition of this report. The relationships were developed from reported costs of unit processes included in chemical, refinery, petrochemical, and, in some cases, municipal waste treatment systems. A generalized scheme can thereby be formulated, which summates the individual process costs, including 35 to 45 percent of the subtotal, to account for related appurtenances and engineering. Estimated costs that would be incurred by the organic chemicals industry in attaining various levels of pollution abatement over a five-year period have been prepared (88).

PRIMARY TREATMENT

Capital cost relationships developed for equalization tanks, neutralization, and primary clarification facilities have been reported (36). Representations for gravity oil separators (20) indicate a

TABLE 16

SUGGESTED BASIS FOR COSTING UNIT PROCESSES

Type of Treatment	Design Basis	Construction Cost Basis	Operational Cost Basis
Pre- or Primary Treatment:			
Equalization	Volume	Cost/Volume	-
Neutralization	Waste Flow	Cost/Waste Flow	Acidity or Alkalinity
Oil Separation	Waste Flow-Overflow Rate	Cost/Waste Flow	-
Sedimentation	Overflow Rate	Cost/Surface Area	-
Biological Treatment:			
Waste Stabilization Ponds	Waste Flow-Surface Loading	Cost/Surface Area	-
Aerated Lagoons	Waste Flow-Organic Loading	Cost/Volume	-
Activated Sludge (Aeration tanks)	Waste Flow-Organic Loading	Cost/Volume	-
*Mechanical Surface (Aeration equipment)	Total HP	Cost/Volume	-
Secondary Clarifier	Overflow Rate	Cost/Surface Area	
Trickling Filter	Waste Flow-Organic Loading	Cost/Filter Volume	-

TABLE 16 (Continued)

SUGGESTED BASIS FOR COSTING UNIT PROCESSES

Type of Treatment	Design Basis	Construction Cost Basis	Operational Cost Basis
Ultimate Disposal:			
Deep Well Injection - Surface Treatment	Waste Flow	Cost/Waste Flow	-
Deep Well Injection	Waste Flow-Depth	Cost/Waste Flow	-
Incineration	Waste Flow-Heat Content	Cost/Waste Flow	-

* As Used in Aerated Lagoons and Activated Sludge

TABLE 16 (Continued)

SUGGESTED BASIS FOR COSTING UNIT PROCESSES

Type of Treatment	Design Basis	Construction Cost Basis	Operational Cost Basis
Tertiary Treatment:			
Ion Exchange	Waste Flow	Cost/Waste Flow	-
Carbon Adsorption	Waste Flow	Cost/Waste Flow	-
Miscellaneous Processes:			
Gas Stripping	Waste Flow	Cost/Waste Flow	Air or Stream Usage
Coagulation	Waste Flow	Cost/Waste Flow	Chemical Requirements
Sludge Handling and Disposal:			
Thickening	Mass Loading	Cost/Thickener Volume	-
Flotation Thickening	Air/Solids Ratio-Overflow Rate	Cost/Surface Area	-
Vacuum Filtration	Filter Loading	Cost/Area of Filter	-
Centrifugation	Waste Flow and Solids Loading	Cost/Waste Flow	HP

decrease in the unit capital cost for separators with increasing flow volumes to a value of approximately 0.7 MGD, at which point the unit cost remains virtually constant with flow.

BIOLOGICAL TREATMENT PROCESSES

Capital cost relationships for lagoons, aerated lagoons, and activated sludge basins have been reported (36). The cost of the lagoon or stabilization pond is highly dependent on the land cost; thus, the correlation developed can only be considered as approximate. Large mechanical surface aerators are more economical than small units based on the same total power requirements. However, mixing considerations often necessitate the use of smaller units. Secondary clarifier costs parallel the cost required for primary clarifiers (36). The unit cost of trickling filters related to waste flow has been graphically developed from several sources (20; 34; 41; 110). The dispersion of reported values is primarily attributable to differences in the organic loadings applied to the various filters. A tabulation of reported daily operating costs for biological treatment facilities in terms of volume treated and pounds of pollutant is given in Table 17.

TERTIARY TREATMENT PROCESSES

At present, tertiary treatment of petrochemical wastes is not commonly practiced. However, cost relationships for the treatment of municipal effluents using ion exchange and carbon adsorption methods have been reported (99). A method has been suggested which uses these relationships to estimate chemical and petrochemical flows (36). This approach considers correcting the flow according to the following expressions:

Ion exchange -

$$\left[\text{Corrected flow}_{\text{Ind. Waste}}\right] = \left[\text{flow}_{\text{Mun. Waste}}\right] \left[\frac{\text{COD}_{\text{Ind.}}}{\text{COD}_{\text{Mun.}}}\right] \quad 0.75$$

Carbon adsorptions -

$$\left[\text{Corrected flow}_{\text{Ind. Waste}}\right] = \left[\text{flow}_{\text{Mun. Waste}}\right] \left[\frac{\text{Total Dissol. Solids}_{\text{Ind.}}}{350}\right] 0.75$$

The corresponding capital costs for the corrected flows can then be determined.

SLUDGE HANDLING AND DISPOSAL PROCESSES

Capital cost relationships for sludge handling using flotation thickening (20) and vacuum filtration (99) have been reported. A cost relationship for total sludge disposal versus flow rate based on

TABLE 17

OPERATING COSTS - WASTE TREATMENT PLANTS

(Reference 34)

Industry	Type of Treatment	Daily Operating Costs $/MG	 $/1,000 lb Pollutant	No. Plants Report-ing	Solids Disposal
Refinery	Primary-includes oil separation, coagulation, flotation, and sedimentation	126-160	26-150 (COD)	4	Vacuum Filter Landfill Incineration
	Secondary-				
	Activated Sludge	161	292 (COD)	1	Landfill
	Aerated Lagoon	22	9 (COD)	1	-
	Extended Aeration	28	14 (COD)	1	Holding Ponds
Chemical	Primary-all types including oil separation, coagulation, flotation sedimentation, neutralization, and equalization	11-1,540	3-40 (S.S.)	11	Landfill Incineration Vacuum Filter Lagoons
	Secondary				
	Aerated Lagoon	31-1,160	6-477 (BOD)	4	Landfill

TABLE 17 (Continued)

OPERATING COSTS - WASTE TREATMENT PLANTS

Industry	Type of Treatment	Daily Operating Costs		No. Plants Reporting	Solids Disposal
		$/MG	$/1,000 lb Pollutant		
Chemical (Cont.)	Secondary (Cont.)				
	Activated Sludge				
	Conventional	1,580	100 (BOD)	1	-
	Extended Aeration	221-276	7-734 (BOD)	5	Landfill, Lagoon
	Contact Stabilization	16-211	23-106 (BOD)	2	Landfill
	Trickling Filter	780-2,050	49-3,750 (BOD)	2	Lagooning
	Facultative Pond	163	39 (BOD)	1	Burning
	Combination				
	Trickling filter and activated sludge	334-378	28-245 (BOD)	2	Landfill

questionnaire information reported by the chemical and petroleum industries has been developed (36). "Total sludge disposal" included aerobic digestion, sludge thickening, vacuum filtration or centrifugation, and final disposal.

ULTIMATE DISPOSAL

The cost of incinerating waste liquids and slurries based on waste flow has been reported (37). This relationship includes operational and capital costs based on a 20-year amortization schedule.

The petroleum refineries reporting to a 1965 survey indicated that the total replacement cost for their waste treatment facilities would be $156,000,000 (14). This report also indicated that 134 refineries are planning future treatment facilities and process modifications which will cost $129,500,000. A similar report from the chemical industry showed a present investment of $263,600,000 in waste treatment plants, with facilities costing approximately $70,000,000 planned for the next five years (14).

It is possible for industry to experience a direct economic return through water reuse and product recovery. In many instances, contaminants can be removed less expensively in the plant than at the treatment facility. These and other factors merit an engineering and economic review, the implementation of which may produce a monetary return to the industry.

REFERENCES

1. Aalund, L., "Petrochemical Activity Hits a New High Around the World," The Oil and Gas J., v. 65, p. 108 (Sept. 4, 1967).

2. Adinoff, J., "Disposal of Organic Chemical Wastes to Underground Formations," Ind. Wastes, v. 1, n. 1, p. 4944 (Sept.-Oct. 1955).

3. Anderson, R. D. and Hansen, R. D., "Phenol Sorption on Ion Exchange Resins," Ind. & Engr. Chem., v. 47, p. 71 (1955).

4. Anon., 1954 Census of Manufacturers: Industrial Water Use Supplement, U. S. Dept. of Commerce, Bureau of the Census, Bull. MC-209 Supp., Washington, D. C. (1957).

5. Anon., 1958 Census of Manufacturers, Summary of Statistics, Vol. 1, U. S. Dept. of Commerce, Bureau of the Census, Washington, D. C. (1961).

6. Anon., Committee Report, Task Group 245, or "Survey of Ground Water Contamination and Waste Disposal Practices," J. AWWA, v. 52, n. 9, p. 1211 (Sept. 1960).

7. Anon., "Huge Global Petroleum Gains Forecast," The Oil and Gas J., v. 64, p. 180 (May 9, 1966).

8. Anon., Manual on Disposal of Refinery Wastes, Vol. I, "Waste Water Containing Oil," American Petrol. Inst., New York, N. Y. (1953).

9. Anon., Manual on Disposal of Refinery Wastes, Vol. III, "Chemical Wastes," American Petrol. Inst., New York, N. Y. (1958).

10. Anon., "Petrochemical Handbook 1967," Hydrocarbon Processing, v. 46, p. 11 (1967).

11. Anon., "Selected Process Flow Sheets for Petrochemicals," The Oil and Gas J., v. 36, n. 36, p. 107 (1964).

12. Anon., Standard Methods for the Examination of Water and Wastewater, American Public Health Assoc., New York, N. Y., 12th Edition (1965).

13. Anon., Union Carbide Puts Corporate Muscle in Pollution Fight," The Oil and Gas J., v. 64, n. 50, p. 132 (1966).

14. Anon., Water in Industry, National Assoc. of Manufacturers and Chamber of Commerce of the U. S., New York and Washington, D. C. (1965).

15. Anon., "What Puts Zip in Petrochemicals," Business Week, p. 40 (Dec. 17, 1966).

16. Anon., "Why Petrochemicals Are Appealing," Business Week, Special Rept., p. 56 (Sept. 3, 1960).

17. Baker, R. A., "Odor Effects of Aqueous Mixtures of Organic Chemicals," J. WPCF, v. 35, n. 6, p. 728 (June 1963).

18. Baker, R. A. and Malo, B. A., "Water Quality Characteristics-Trace Organics," ASCE-Proc. v. 93 (J.San. Engr. Div.) n. SA6, p. 41 (Dec. 1967).

19. Beak, T. W., Discussion of "Behavior of Fish Exposed to Toxic Substances," Advances in Water Pollution Research, Vol. I, p. 38 (1965).

20. Beychok, M. R., Aqueous Wastes from Petroleum and Petrochemical Plants, John Wiley & Sons, London (1967).

21. Brady, S. O., "Taste and Odor Components in Refinery Effluents," Air & Water Conservation Session, API, 33rd Mid-Year Meeting, Philadelphia, Pa. (1968).

22. Brunner, C. A. and Stephan. D. G., "Foam Fractionation," Ind. & Engr. Chemistry, v. 57, n. 5, p. 40 (May 1965).

23. Brush, A. E. and Wheeler, W. W., "Treatment of a Petrochemical Waste on a Trickling Filter," Proc. 2nd Ind. Water & Waste Conf., Texas Water Poll. Control Assoc., Austin, Texas, p. 171 (1962).

24. Butler, P. E., et. al., "Modern Instrumental Techniques in Structure Elucidation of Products Derived from Petrochemicals," Environ. Sci. & Tech., v. 1, n. 4, p. 315 (April 1967).

25. Cairns, J., Jr., "Environment and Time in Fish Toxicity," Ind. Wastes, v. 2, n. 1, p. 1 (Jan., Feb. 1957).

26. Cairns, J., Jr., "Biological Concepts and Industrial Waste Disposal Problems," Proc. 20th Ind. Wastes Conf., Purdue Univ., p. 49 (1965).

27. Chipperfield, P. N. J., "Performance of Plastic Filter Media in Industrial and Domestic Waste Treatment," *J. WPCF*, v. 39, n. 11, p. 1860 (Nov. 1967).

28. Clark, F. E., "Industrial Re-Use of Wastewater," *Ind. & Engr. Chemistry*, v. 54, n. 2, p. 18 (Feb. 1962).

29. Coe, R. C., "Bench Scale Method for Treating Waste by Activated Sludge," *Petrol Proc.*, v. 7, p. 1128 (Aug. 1952).

30. Dean, B. T., "Nylon Waste Treatment," *J. WPCF*, v. 33, n. 8, p. 864 (Aug. 1961).

31. DeRopp, N. W., "Chemical Waste Disposal at Victoria, Texas, Plant of the DuPont Company," *Sew. and Ind. Wastes*, v. 23, n. 2, p. 194 (1951).

32. Dickerson, B. W. Campbell, C. J. and Stankard, M., "Further Operating Experiences on Biological Purification of Formaldehyde Wastes," *Proc. 9th Ind. Waste Conf.*, Purdue Univ., p. 331 (1954).

33. Dickerson, B. W. and Laffey, W. T., "Pilot Plant Studies of Phenolic Wastes from Petrochemical Operarions," *Proc. 14th Ind. Waste Conf.*, Purdue Univ., p. 780 (1959).

34. Eckenfelder, W. W., Jr., "Effluent Quality and Treatment Economics for Industrial Wastewater," Rept. to FWPCA, Washington, D. C. (1967).

35. Eckenfelder, W. W., Jr., *Industrial Water Pollution Control*, McGraw-Hill Book Co., New York, N. Y. (1966).

36. Eckenfelder, W. W., Jr., *et. al.*, Unpublished Rept. (1968).

37. Eckenfelder, W. W., Jr., Kleffman, R. and Walker J., "Some Theoretical Aspects of Solvent Stripping and Aeration of Industrial Wastes," *Proc. 11th Ind. Waste Conf.*, Purdue Univ., p. 14 (1956).

38. Eisenhauer, H. R., "Oxidation of Phenolic Wastes," *J. WPCF*, v. 36, n. 9, p. 1116 (Sept. 1964).

39. Englebrecht, R. S. and Ewing, B. B., "Treatment of Petrochemical Wastes by Activated Sludge Process," *Proc. 2nd Ind. Water and Waste Conf.*, Texas Water Poll. Control Assoc., Austin, Texas, p. 149 (1962).

40. Ettinger, M. B., "Proposed Toxicity Screening Procedure for Use in Protecting Drinking Water Quality," J. AWWA, v. 52, n. 6, p. 689 (June 1960).

41. Forbes, M. C. and Witt, P. A., "Estimate Cost of Waste Disposal," Hydrocarbon Processing, v. 44, n. 8, p. 153 (1965).

42. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (Jan. 1967).

43. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (Feb. 1967).

44. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (May 1967).

45. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (July 1967).

46. Gaudy, A. F., Jr., Englebrecht, R. S. and Turner, B. G., "Stripping Kinetics of Volatile Components of Petrochemical Wastes, J. WPCF, v. 33, n. 4, p. 382 (April 1961).

47. Giebler, G., "Treatment of Wastewaters of the Pesticide Industry," Von Wasser, v. 25, p. 197 (1958).

48. Gloyna, E. F. and Ford, D. L., "Injection of Wastewaters into Disposal Wells," Unpublished Rept. (1966).

49. Gloyna, E. F. and Malina, J. F., Jr., "Petrochemical Wastes Effect on Water," Ind. Water & Wastes, pt. 1, Sept.-Oct. 1962,pt. 2, Nov.-Dec. 1962, pt. 3, Jan.-Feb. 1963, pt. 4, March-April 1963.

50. Gossom, W. J. and Stevens, J. I., "The Near Ultimate Disposal of Refinery Wastes," Tech. Paper 65-42. Rocky Mountain Regional Meeting. Natl Petrol. Refiners Inst., Casper, Wyoming (1965).

51. Green, R. V. and Moses, D. V., "Destructive Catalytic Oxidation of Aqueous Waste Materials," Sew. and Ind. Wastes, v. 24, n. 3, p. 288 (1952).

52. Hatch, L. F., The Chemistry of Petrochemical Reactions, Gulf Pub. Co., Houston, Texas (1955).

53. Heller, A. M., et. al., "Some Factors in Selection of a Phenol Recovery Process," Proc. 12th Ind. Waste Conf., Purdue Univ., p. 103 (1957).

54. Henkel, H. O., "Deep Well Disposal of Chemical Waste Water," Proc. of the 5th Annual Sanitary and Water Resources Engr. Conf., Vanderbilt Univ., Tech. Rept. 9, p. 26 (1966).

55. Holland, H. R. and Clark, F. R., "A Disposal Well for Spent Sulphuric Acid from Alkylating Iso-Butane and Butylenes," Proc. 19th Ind. Waste Conf., Purdue Univ., v. 49, n. 1, p. 195 (1964).

56. Huang, J. C. and Gloyna, E. F., "Effects of Toxic Organics on Photosynthetic Reoxygenation," Center for Research in Water Resources Rept. No. 20, The Univ. of Texas, Austin,(1967).

57. Hueper, W. C., "Cancer Hazards from Natural and Artificial Water Pollutants," Proc. Conf. on Physiol. Aspects of Water Quality, U S P H S , Washington, D. C., p. 181 (1960).

58. Hutner, S. H., Baker, H., Arronson, A. and Zahalsky, A. C., "Bacetria-Protozoa as Indicators in Purifying Water," Biological Problems in Water Pollution - Third Seminar 1962, R. A. Taft San. Engr. Center, Cincinnati, Ohio, p. 45 (1965).

59. Huber, L., "Disposal of Effluents from Petroleum Refineries and Petrochemical Plants," Proc. 22nd Ind. Wastes Conf., Purdue Univ. (1967).

60. Hyde, A. C., "Chemical Plant Waste Treatment by Ten Methods," J. WPCF, v. 37, n. 11, p. 1486 (Nov. 1965).

61. Ishio, S., "Behavior of Fish Exposed to Toxic Substances," Advances in Water Pollution Research, 2nd Conf., Vol. I, p. 19 (1965).

62. Karger, B. L. and Rogers, L. B., "Foam Fractionation of Organic Compounds," Anal. Chemistry, v. 33, n. 9, p. 1165 (Aug. 1961).

63. Klein, L., River Pollution II. Causes and Effects, Butterworths & Co., Ltd., London (1962).

64. Klippel, R. W., Rept. on Pollution Control Planning for the Guayama Petrochemical Complex, Phillips Petroleum Co., Bartlesville, Oklahoma (1966).

65. Klotzman, M. and Vier, B., "Celanese Pumps Wastes into Disposal Wells," The Oil and Gas J., v. 64, n. 15, p. 84 (1966).

66. Kneese, A. V., Water Pollution - Economic Aspects and Research Needs, Resources for the Future, Inc., Washington, D. C. (1962).

67. Koenig, L., "Ultimate Disposal of Advanced-Treatment Waste," U S P H S, Publication No. 999-WP-3, Cincinnati, Ohio (1963).

68. Lewis, W. L. and Martin, W. C., "Remove Phenols from Waste Waters," Hydrocarbon Processing, v. 46, n. 2, p. 131 (Feb. 1967).

69. Ling, J. T., "Pilot Study of Treating Chemical Wastes with Aerated Lagoon," J. WPCF, v. 35, n. 8, p. 963 (Aug. 1963).

70. Lively, L., Rosen, A. A. and Mashni, C. I., "Identification of Petroleum Products in Water," Proc. 20th Ind. Waste Conf., Purdue Univ. (1965).

71. Lockett, D. E., "Subsurface Disposal of Industrial Waste Waters," Presented at Southwestern Petroleum Short Course, Dept. of Petro. Engr., Texas Tech. College, Lubbock, Texas (April 1967).

72. Ludzack, F. J. and Ettinger, M. B., "Chemical Structures Resistant to Aerobic Biochemical Stabilization," J. WPCF, v. 32, n. 11, p. 1173 (Nov. 1960).

73. Ludzack, F. J., Scheffer, R. B. and Bloomhuff, R. N., "Experimental Treatment of Organic Cyanides by Conventional Processes," J. WPCF, v. 33, n. 5, p. 492 (May 1961).

74. McGauhey, P. H. and Klein, S. A., "Removal of ABS from Sewage," Public Works, v. 92, n. 5, p. 101 (May 1961).

75. McGrath, H. G., "Petrochemicals to Star '60's," The Oil and Gas J., v. 59, p. 129 (Nov. 20, 1961).

76. McRae, A. D., "Disposal of Alkaline Wastes in the Petrochemical Industry," Sew. and Ind. Wastes, v. 31, n. 6, p. 712 (July 1959).

77. Mellon, M. G., "Detection and Analysis of Chemicals in Water. I. Inorganic Constituents," Proc. Conf. on Physiol. Aspects of Water Quality, U S P H S, Washington, D. C., v. 27 (1960).

78. Mencher, S. K., "Minimizing Waste in the Petrochemical Industry," Chem. Engr. Progress, v. 63, n. 10, p. 80 (Oct. 1967).

79. Mills, E. J. and Stack, V. T., "Biological Oxidation of Synthetic Organic Chemicals," Proc. 8th Ind. Waste Conf., Purdue Univ. p. 492 (1953).

80. Mills, R. E., "Development of Design Criteria for Biological Treatment of an Industrial Effluent Containing 2,4-D Waste Water," Proc. 14th Ind. Waste Conf., Purdue Univ., p. 340 (1959).

81. Pahren, H. R. and Bloodgood, D. E., "Biological Oxidation of Several Vinyl Compounds," *J. WPCF*, v. 33, n. 3, p. 233 (May 1961).

82. Paynter, O. E., "Chronic Toxicity of Dodecylbenzene Sodium Sulfonate," *Proc. Conf. on Physiol Aspects of Water Quality*, U S P H S., Washington, D. C. p. 175 (1960).

83. Phillips, C., Jr., "Treatment of Refinery Emulsions and Chemical Wastes," *Ind. & Engr. Chemistry*, v. 46, p. 300 (1954).

84. Pruessner, R. D. and Mancini, J., "Extended Aeration Activated Sludge Treatment of Petrochemical Waste at the Houston Plant of Petro-Tex Chemical Corporation," *Proc. 21st Ind. Waste Conf.*, Purdue Univ., v. 50, n. 2, p. 591 (1966).

85. Querio, C. W. and Power, T. J., "Deep Well Disposal of Industrial Wastewater," *J. WPCF*, v. 34, n. 2, p. 126 (1962).

86. Remy, E. D. and Lauria, D. T., "Disposal of Nylon Wastes," *Proc. 13th Ind. Waste Conf.*, Purdue Univ., v. 43, n. 3, p. 596 (1958).

87. Rice, J. K., "Eliminate Waste Water Discharge," *Petro/Chem Engineer*, p. 21 (Oct. 1966).

88. Rice, C. W. and Company, Eckenfelder, W. W., Jr. and Associates and Weston, R. F., Inc., *Projected Wastewater Treatment Costs in the Organic Chemicals Industry*, Unpublished Rept. to the F W P C A (January 1969).

89. Ruggles, W. C., "Basic Petrochemical Processes as Waste Sources," *Sew. and Ind. Wastes*, v. 31, n. 3, p. 274 (March 1959).

90. Ruchhoft, C. C., *et. al.*, "Waste Disposal in Petroleum Industry," *Ind. & Engr. Chemistry*, v. 46, n. 2, p. 283 (Feb. 1954).

91. Sadow, R. D., "The Treatment of Zefran Fiber Wastes," *Proc. 15th Ind. Waste Conf.*, Purdue Univ., p. 395 (1960).

92. Sadow, R. D., "Waste Treatment at a Large Petrochemical Plant," *J. WPCF*, v. 38, n. 3, p. 428 (March 1968).

93. Sawyer, F. G., "Best Picks for '66: Petrochemicals," *Hydrocarbon Processing*, v. 46, n. 1, p. 161 (Jan. 1966).

94. Senate Reports, *Future Water Requirements of Principal Water-Using Industries*, Select Committee on Natl. Water Resources, 86th Congress Committee Print No. 8 (1960).

95. Shannon, E. S., "Handling and Treating Petrochemical Plant Wastes: A Case History," Water & Sew. Works, v. 111, n. 5, p. 240 (1964).

96. Sherwood, P. W., "First-Generation Chemicals Today," World Petrol. Annual Refinery Review, v. 35, n. 8, p. 61 (1964).

97. Sherwood, P. W., "Whiter Petrochemicals?" The Oil and Gas J., p. 73 (Dec. 16, 1963).

98. Singleton, K. G., "Biological Treatment of Waste Water from Synthetic Resin Manufacture," Proc. 21st Ind. Waste Conf., p. 62, Purdue Univ. (1966).

99. Smith, R., "Cost of Conventional and Advanced Treatment of Wastewater," J. WPCF, v. 40, n. 9, p. 1546 (Sept. 1968).

100. Stanley, H. M., The Petroleum-Chemicals Industry, Lecture Series 1963, n. 4, The Royal Inst. of Chemistry (1963).

101. Steen, J. H., Majewski, F. M. and Iezzi, T., "Waste Treatment at a Large Chemical Manufacturing Plant," Sew. and Ind. Wastes, v. 28, p. 866 (July 1956).

102. Stein, K. C., et. al., "Oxidation of Hydrocarbons on Simple Oxide Catalysts," Air Poll. Control Assoc., v. 10, n. 4, p. 275 (Aug. 1960).

103. Stephenson, R. M., Introduction to the Chemical Process Industry, Reinhold Pub. Corp., New York, N. Y. (1966).

104. Stockton, J. R., Arbingast, S. A., Henshaw, R. C., Jr. and Dale, A. G., Water for the Future, Vol. II, Bureau of Business Research, The Univ. of Texas, Austin, p. 30 (1959).

105. Taylor, E. F., et. al., "Orlon Manufacturing Wastes Treatment," J. WPCF, v. 33, n. 10, p. 1076 (Oct. 1961).

106. Teal, J. L., "The Control of Waste Through Fish Taste," American Chem. Society, Natl. Meeting (1959).

107. Thirumurthi, D. and Gloyna, E. F., "Relative Toxicity of Organics to Chlorella pyrenoidosa," Center for Research in Water Resources Rept. No. 4, The Univ. of Texas, Austin (1965).

108. Todd, D. K., Ground Water Hydrology, John Wiley & Sons, Inc., New York, N. Y., p. 85 (1959).

109. Warner, D. L., "Deep Industrial Waste Injection Wells in the United States, A Summary of Pertinent Data," Rept. to FWPCA, Cincinnati, Ohio (1966).

110. Wilson, I. S., "The Treatment of Chemical Wastes," Waste Treatment, Isaac, P. C. G., ed., Pergamon Press, London, p. 206 (1960).

111. Word, J. C., Wright, M. V. and Klippel, R. W., "Treating Complex Petroleum Wastes at Borger, Texas," paper from Phillips Petroleum Co.

112. Wright, E. R., "Secondary Petrochemical Process as Waste Sources," Sew. and Ind. Wastes, v. 31, n. 5, p. 575 (May 1959).

113. Wright, R. L,, "Treatment of Petro-Chemical Wastes at Port Lavaca, Texas," Sew. and Ind. Wastes, v. 29, p. 1033 (Sept. 1957).

114. Weyermuller, G. and Davidson, J. A., "Submerged Combustion Prevents Polymer-Waste Problem," Chem. Processing (Feb. 1958).

115. Vier, B. B., "Celanese Deep Well Disposal Practice," Proc. 7th Ind. Water and Waste Conf., Texas WPCA (1967).

116. Vrablick, E. F., "An Evaluation of Circular Gravity Type Separation and Dissolved - Air Flotation for Treating Oil Refinery Waste Water," Proc. 12th Ind. Waste Conf., Purdue Univ., p. 72 (1957).

117. Anon., The Petroleum Handbook, Shell International Petroleum Co., Ltd., 5th Edition, Balding and Mansell, Ltd., eds., London (1966).

118. Anon., Drinking Water Standards, U. S. Public Health Service Publication No. 956 (1962).

119. Bland, W. F. and Davidson, R. L., eds., Petroleum Processing Handbook, McGraw-Hill, New York (1967).

120. Kinney, J. E., "Fusing the Phenol Frenzy," Proc. 15th Ind. Waste Conf., Purdue Univ., p. 29 (1960).

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27 *Abstract*
Each of the major processes developed by the industry should be studied with the objective of evaluating the trends in plant locations, effects on area-wide water quality, and treatment requirements. Since there will be no significant changes in petrochemical feedstocks, the patterns of feedstock usage should be monitored and major changes evaluated in terms of the water use and water reuse requirements, potential pollution problems, and product development. Because the main contribution to environmental pollution from the petrochemical industry emanates from process waste streams, comparative cost analyses should be made on typical recycle (feedstock) practices and on associated wastewater treatment requirements. A comprehensive and coordinated evaluation program should be developed specifically for standardizing the characterization techniques of wastewaters containing complex and undefinable petrochemical and related wastewater constituents. Large volumes of wastewater could be reused within the plants with varying degrees of treatment; most wastewaters require some form of primary product recovery and treatment, oil removal, settleable solids removal, and reduction in the organic content. Master plans for in-plant wastewater collection should include facilities to segregate process waste from less contaminated streams. Problem areas in the physical, chemical and biological treatment processes, as well as disposal methods, are listed. A detailed and basic study should be initiated to evaluate the cost of treating wastes from single plants or process streams with combined wastes from several plants.

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